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OPTIMUM WORKING FLUIDS FOR AUTOMOTIVE RANKINE ENGINES.
VOLUME II. TECHNICAL SECTION

Monsanto Research Corporation

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16. ABSTRACT

The objective of the work was to determine the best working fluids available for the automotive Rankine engine application. Specific guidelines were established for the fluid screening process. The details of the screening and testing procedures are presented. As a result of the various criterion-guided experimental and computational studies, two final candidate fluids were identified: RC-1: A 60/40 mole percent mixture of pentafluorobenzene/hexafluorobenzene; RC-2: A 65/35 mole percent mixture of water/2-methylpyridine. Both fluids are liquid to -40°F and meet critical performance criteria for both reciprocating and turbine engines, although neither completely satisfies all requirements and criteria. The experimental program to characterize them is presented. Other topics which relate to the RC-1 and RC-2 fluid are as follows: (1) cycle calculation, (2) stability/compatibility, (3) rat inhalations studies, (4) flammability (5) lubrication and lubricants. The results of the tests are presented and evaluated. Fluid RC-1 comes nearest to satisfying the automotive organic working fluid requirements and goals set by AAPSDD. Fluid RC-2 is a back-up candidate for automotive use, either in a turbine or reciprocating engine. Many organic fluids possess the state and thermodynamic properties needed to attain engine performance goals but are eliminated for other reasons. Other conclusions and recommendations are presented.

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a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
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Rankine Cycle	Mixed Fluorobenzenes	21 G
Engines	Aqueous Pyridines	21 E
Design		14 B
Turbines		7 C
Computer Programs		
Reciprocating Engines		

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1. INTRODUCTION

This is the second of a four-volume final report on a research program performed by Monsanto Research Corporation for the U.S. Environmental Protection Agency, Advanced Automotive Power Systems Development Division (AAPSDD) under contract 68-04-0030. The objective of the work was to determine the best working fluids for Rankine cycle automotive power plants.

The Rankine engine has been identified by EPA as a potential alternative to the internal combustion automotive engine in the event the internal combustion engine can not satisfy the 1975/76 Federal Emission Standards. Development work has been proceeding on the Rankine engine, as well as other alternative power plants, under the direction of AAPSDD since initiation of the Clean Air Act Amendments of 1970.

In a Rankine cycle power plant, the working fluid, which is repeatedly vaporized, expanded and recondensed, plays a key role in determining the competitiveness of the system. The thermodynamic, chemical and physical properties of the fluid have a strong influence on the power plant efficiency, materials of construction, component weight and size, the degree of hazard, if any, and to some extent the power plant cost. Therefore, to make certain that the Rankine engine could be evaluated at its greatest potential, this study program was initiated to search out the best fluids currently available for the automotive Rankine engine application.

To accomplish this objective, specific guidelines were established for the fluid screening process. These guidelines are outlined in the work statement of Appendix A and summarized as follows:

Minimum Carnot Cycle Efficiency	42%
Minimum Rankine Cycle Efficiency	30%
Maximum Cost to Owner, 5 yr period	$100
Melting Point	≤-40°F
Health Hazards	Nil
Fire and Explosion Hazards	Nil
Environmental Hazards	Nil

The above restraints were contractual requirements and were intended to approximate the upper limit of what could be achieved with presently known materials and current technology. The results indeed reveal that the criteria were well chosen, as only two possible fluids from over 100 candidates survived the screening process, and these did not totally satisfy all of the stated requirements. In reviewing the results it should be kept in mind that less stringent or different selection criteria could very well have led to the selection of other candidates.

The order of presentation of the technical results in this report has been inverted for the convenience of the reader. Results specific to the two final candidate fluids are concentrated in Section 5, whereas the prior search leading to the choice of the two candidates is the subject of Section 6. The chronological sequence of the report is through sections 1, 6, 5, 2, 3, 4.

Companion Volume IV of this final report covers system optimization studies by Sundstrand Aviation (under subcontract to Monsanto Research Corporation) of each of the two final candidate fluids, one in a turbine, the other in a reciprocating power plant.

2. SUMMARY

Four major tasks were undertaken in response to the basic contract, namely:

1. Establishing working fluid selection criteria (Section 6.1)
2. Searching for and screening a large group of fluid candidates (Section 6.2 through 6.11)
3. Developing a comprehensive data base for the most promising two candidates (Section 5)
4. Predicting optimum engine designs, one reciprocating and one turbine, involving the two preferred working fluids (Volume IV)

Selection criteria were first established to provide as quantitative as possible a basis for seeking and then accepting or rejecting members of a broad collection of likely fluids. The criteria covered fluid availability, physical properties, thermal stability, thermodynamic and cycle efficiency and utility in principal engine types. It was not deemed practical to quantize all criteria, nor to be rigidly proscribed by those that were quantized. The criteria were of greatest utility in permitting early elimination of entire chemical classes of materials from further consideration. As one example, chlorine-containing organics were eliminated as a class when no members were found able to long survive a 720°F steel ampoule screening test. Other examples can be found in Section 6.

The search for candidate working fluids centered on pure compounds boiling (at atmospheric pressure) in the range of 150 to 250°F and freezing below 68°F. On the bases of availability and expected thermal stability, about 110 pure fluids were obtained and subjected to the 720°F steel ampoule test. Those few surviving 200 hours without serious decomposition were then subjected to an "I-factor" test, a criterion designed to uncover fluids capable of high efficiency cycle operation without requiring prohibitively large regenerative heat exchangers. Computer-aided predictions of vapor heat capacities and heats of vaporization provided the I-factor values.

The search for working fluids was not confined to pure compounds. Mixed (or complex) fluids were included to permit more control over freezing points and thermodynamic characteristics. Thermodynamic prediction techniques were broadened to include non-ideal as well as ideal solutions. Graphing of temperature-entropy diagrams for both simple and complex fluids was mechanized.

As a result of the various criterion-guided experimental and computational studies, two final candidate fluids were identified:

RC-1: A 60/40 mole percent mixture of pentafluorobenzene/hexafluorobenzene;

RC-2: A 65/35 mole percent mixture of water/2-methylpyridine

Both fluids are liquid to -40°F and meet critical performance criteria for both reciprocating and turbine engines, although neither completely satisfies all requirements and criteria.

After identifying the two final candidates, an extensive experimental program was undertaken to characterize them. Liquid physical properties measured included vapor pressure, density, viscosity, thermal conductivity, flow point and heat capacity. These data, combined with literature data available for the pure components of the candidates, were then used to predict other properties of the mixtures, notably vapor heat capacity, viscosity, and thermal conductivity. Complete tables of thermodynamic variables were next computed using a Redlich-Kwong equation of state specially modified to handle non-ideal solutions. Temperature-entropy diagrams were also computer-generated.

Predictions of fluid performance in both an ideal and a real Rankine cycle were next prepared and compared with system restrictions. Both qualified in all respects except that RC-2 failed the 30% ideal cycle efficiency criterion.

Both candidates were subjected to 1000-hour dynamic loop testing under conditions of temperature (720°F max.) and pressure (1000 psig max.) simulating ultimate use. In this test, the RC-1 candidate passed with only a trace of decomposition, whereas the RC-2 candidate failed due to excessive corrosion of the SAE 4130 steel tubing utilized in the vapor generator. A more corrosion-resistant steel or steel finish is required before RC-2 can be exploited as an automotive working fluid.

Compatibilities of the candidates with a wide range of both metallic and non-metallic materials were determined in a series of 300°F ampoule exposure tests. The choice of wetted materials is wider for RC-1 than for RC-2.

A battery of animal acute exposure tests were performed to gauge the acute toxicities of the final candidates. Included were rat inhalation, rat oral feeding, rabbit skin absorption, rabbit skin irritation, and rabbit eye irritation tests. Special attention was given to vapor inhalation as the most likely avenue of public exposure. Predictions of likely dosages to be encountered in a "worst-case" accident were performed to compare with the animal inhalation data. Additionally, experiments were performed to identify products of combustion of the working fluids exposed to a propane flame.

Flammability parameters were measured, including flash and fire points, autoignition temperature, and ignition-explosion character. RC-1 was found practically non-flammable. RC-2 is flammable, although the presence of water does materially reduce the energy release below typical fuel values.

Heat-stable lubricants were sought for each fluid. Only synthetics were found to withstand the 720°F exposure conditions. A biphenyl-terphenyl eutectic was defined and tested with both candidates and with a wide variety of sliding element materials in a special rub-block friction-wear test machine. This lubricant was soluble in both candidates.

A limited program of lubricant synthesis, undertaken to find an RC-2 immiscible lubricant, identified the highly silylated benzenes as possessing the required thermal stability and immiscibility. Two deficiencies of the materials studied were high expected cost and high solidification point.

Future selling prices of the two candidate working fluids were estimated based on economic and technological information available in the open literature. The analysis included, in the case of RC-1, a conceptual plant design employing a fluorination process never practiced at larger than bench scale. Using the projected selling prices, estimates were made of the fluid cost to the Rankine automobile owner over the first five years of ownership. The RC-1 candidate was projected to cost 12% over the contractual limit of $100; whereas the RC-2 candidate can be expected to cost less than the limit.

The last task, that of predicting optimum engine designs corresponding to the two final candidate working fluids, is summarized in Volume IV.

3. CONCLUSIONS

1. No organic or aqueous organic fluids were found to completely satisfy all the requirements established in the contract for Rankine cycle automotive power plant working fluids.

2. Fluid RC-1 comes nearest to satisfying the automotive organic working fluid requirements and goals set by AAPSDD. It meets all of the established performance criteria for both turbine and reciprocating engines, including efficiencies, temperature, pressure and density limitations, and regenerator size. Additionally it is considered fire-safe and unlikely to cause serious injury on accidental human exposure (subject to verification in extended toxicity testing recommended as a follow on). The fluid is quite stable at temperatures to at least 720°F in low-cost system materials, and it is expected to last for at least the 5-year span of initial vehicle ownership. It possesses a distinct advantage over water in not freezing at temperatures down to -40°F. A low cost soluble lubricant is available if needed. The main contractual deficiency of the fluid is its projected cost of no less than $112/over its expected five-year life, as compared to a $100 contract limit. To arrive at the $112 cost it was necessary to assume a) successful advancement of the state of fluorination technology beyond that now practiced, and b) the existence of a 50 million pound per year benzene fluorination plant. Current prices of the higher fluorinated benzenes are many times the projected price. Turning to cycle practicality, the comparatively high flow rate of the RC-1 fluid per net cycle horsepower (related to its higher molecular weight) may be considered a disadvantage despite the lack of a contractual limit. All in all, this fluid is worthy of further development.

3. Fluid RC-2 is a back-up candidate for automotive use, either in a turbine or reciprocating engine. It satisfies all performance criteria except the 30% minimum ideal cycle efficiency.

Even so, the fluid is capable of high efficiency usage in a real cycle with a compact regenerator. Although the fluid is flammable, it is less so than common fuels. In burning it releases considerably less energy because of its water content, and its products of combustion are not hazardous to humans. The fluid itself is unlikely to cause serious injury. It is marginally stable at 720°F in steel. SAE 4130 steel is not a compatible material for boiler tube construction with RC-2. The fluid acts chemically to corrode this steel, forming Fe_3O_4 and hydrogen. A more suitable steel alloy needs to be found before this fluid can be considered a contender with RC-1. Assuming a satisfactory steel were found, the RC-2 fluid would cost the vehicle owner about $100 in the first five years of vehicle life. This presumes three system refills. Traditional lubricants cannot be used with this fluid above 700°F, but low cost synthetics offer promise when mutual solubility is permissible. Synthetic silane lubricants may be considered if immiscibility is mandatory, but further development is needed. Fluidity above -40°F is another feature of importance. The prime ingredient of the fluid is commercially available at low cost now, but in lesser quantity than would be commanded by a million cars-per-year market. RC-2 is worthy of further development only in the unlikely event that candidate RC-1 must be abandoned.

4 4. Many organic fluids posses the state and thermodynamic properties needed to attain engine performance goals. are eliminated for this reason.

5. Very few fluids possess the requisite thermochemical stability in steel at 712°F (and higher). Those that do fall in these categories:

   Aromatics

   Fluoroaromatics

   Aromatic tertiary amines

   Perfluoroaliphatics

   Water

6. Flammability eliminates the aromatics from contention, and places the aromatic tertiary amines in a contingency category. Since the aromatic tertiary amines (or pyridines) are quite flammable and water soluble, their safe usage in automobiles is contingent upon a suitable reduction in flammability effected by mixing with water.

7. An excessive demand for regenerator space to maintain tolerable cycle efficiency rules out the perfluoroaliphatics. This is clearly shown by the I-factor criterion and the supporting cycle calculations.

8. Additional restrictions on vapor pressure, melting point (or "flow" point), cost, and toxicity further narrow the choice to

   mixed fluorobenzens, and

   aqueous pyridines,

   from which categories the final candidates RC-1 and 2 were chosen.

9. The search rationale adopted at the outset was basically sound, although some adjustments were necessary. Particularly valuable features were:

   a. an efficient thermal stability screening program

   b. development and effective use of the I-factor concept for thermodynamic screening - including confirmation via I-factor - efficiency correlations

   c. maximal use of computation throughout, but especially in these areas:

      prediction of thermodynamics of non-ideal/ideal mixtures

      I-factor and physical property predictions

      ideal and real cycle calculations

   d. the concept of progressive advancement of candidates, exposing each to increasingly rigorous examination.

4. RECOMMENDATIONS

Relative to fluid RC-1, it is recommended that:

1. It be considered an acceptable organic fluid for a prototype engine development program.

2. Static thermochemical stability tests be performed to learn how far above 720°F the fluid might be driven.

3. Providing prototype experience is favorable, the fluid be subjected to a carefully planned set of exposure tests in the areas of

chronic inhalation
chronic dermal contact
environmental fate

as necessary to qualify the fluid for widespread use.

4. Encouragement be given to prospective manufacturers to develop the necessary low-cost processes for large scale production.

Relative to fluid RC-2, and assuming abandonment of RC-1, it is recommended that:

5. Additional work be undertaken to find a suitable steel and/or steel passivation technique to avoid the iron-water reaction at high temperature.

6. If appropriate, additional synthesis work be done to finalize an immiscible silane lubricant.

7. A fire hazard simulation be performed, preferably involving a mock-up burner-vapor generator and a simulated high pressure fluid leak.

8. The first three recommendations under RC-1 be followed.

5. FINAL CANDIDATES

5.1 CHOICE AND COMPOSITION

Details of the extensive search for working fluids conforming to the demanding goals of this study are given in Section 6. A brief summary here of the search findings serves to explain the choice of final working fluid candidates.

No all-inorganic fluids were uncovered which were simultaneously compatible with mild steel at 720°F and potentially inexpensive. Inorganic compounds qualifying by melting and/or boiling point are nearly all ionic chlorine-bearing materials which are highly corrosive to low cost metals, especially at high temperature or when wet. (Water itself is an obvious exception)

Close scrutiny of the 140+ organic working fluids entered in the screening process of Section 6 disclosed none likely to fully satisfy all search goals simultaneously. Competitive tradeoffs became painfully evident. Only one way was found to secure high fire resistance simultaneously with good thermal stability at 720°F. That was to incorporate many fluorine atoms on an organic nucleus. But fluorination, especially of aromatics, is inherently expensive. This then threatens the attainment of a 5-year fluid cost of $100 to the automobile owner. Highly fluorinated chain compounds (fluoroalkanes and related) can be found which are stable, firesafe, and potentially less expensive, but all such compounds cited suffer the defect of demanding impossibly bulky regenerative heat exchangers to attain reasonable cycle efficiencies.

Two candidate working fluids were selected for final evaluation and verification based upon two distinctly different rationalizations of the available fluid data and the competitive tradeoffs:

1. A fluid qualifying under the screening criteria most likely to be fire-safe and stable, but with relaxation of the owner cost requirement ($100 in 5 years).
2. A fluid qualifying under the screening criteria most likely to be low-cost and stable, but with relaxation of the goal of non-flammability.

Corresponding to these two rationalizations are the two final candidate working fluids designated as RC-1 and RC-2.

5.1.1 Final Candidate RC-1

The composition of Fluid RC-1 is given in Table 1.

Table 1. RC-1 COMPOSITION

Component	Mol. Wt.	Concentration	
		Mol %	Wgt %
pentafluorobenzene	168.1	60.0	57.5
hexafluorobenzene	186.1	40.0	42.5

Note: Alternate compositions, including proportions of other fluorinated benzenes in addition to, or in lieu of, those listed, are acceptable so long as they conform to flammability, flow point and other requirements

Hexafluorobenzene is an attractive working fluid candidate in its own right because of its outstanding fire resistance and high thermal stability. Alone, however, it crystallizes at 41°F (5°C) and thus fails the -20°F cold start requirement, if not the -40°F no-damage requirement. It is obviously attractive to mix another stable miscible fluid with hexafluorobenzene to reduce the crystallizing point by the requisite amount. Consideration was given to a number of companion fluoro chemicals, especially pentafluoropyridine, octafluorotoluene, FC-75, P-1D, and lower fluorinated benzenes. By far the most attractive of these is the latter class, as exemplified by pentafluorobenzene, because chemicals of this class can be produced simultaneously with hexafluorobenzene in the same chemical processing plant.

The 60-40 mol ratio was selected to place the flow point just under the -40°F temperature specified as the highest permissible cold-damage fluid temperature (refer to Figure 1). If, instead, the flow point had been placed at -20°F (-29°C), the specified highest engine coldstart temperature, the pentafluorobenzene content would have been 52 rather than 60 mol percent. The presence of additional amounts of lower fluorinated benzenes in a commercial fluid would tend to lower the crystallizing point somewhat, permitting a slightly higher hexafluorobenzene content in either case.

The thermal stabilities of the ingredients of this candidate have been established in Section 6.3. Other stable materials considered as components for this candidate, with the reasons for their rejection, were:

- lower fluorinated benzenes - flammability
- fluorinated toluenes - cost
- di(trifluoromethyl)benzenes - I-factor (regen. size)
- perfluoro alkanes, cycloalkanes - I-factor (regen. size)
- pentafluoropyridine - cost, toxicity

5.1.2 Final Candidate RC-2

The composition of Fluid RC-2 is given in Table 2 on page 12. Water is a preferred candidate from several viewpoints, especially cost, hazards, and stability. Two decisive defects for automotive use are lower cycle efficiency than organics at fixed operating temperatures and high freezing point. As with hexafluorobenzene, it is attractive to seek a miscible companion fluid to mix with water to correct its deficiencies. Of all organic materials turned up in the search, only pyridine and its three monomethyl derivatives, 2-, 3- and 4-methylpyridine (also called α-, β- and γ-picoline, respectively), possessed the requisite 720+°F thermal stability and water miscibility. While all the pyridines will

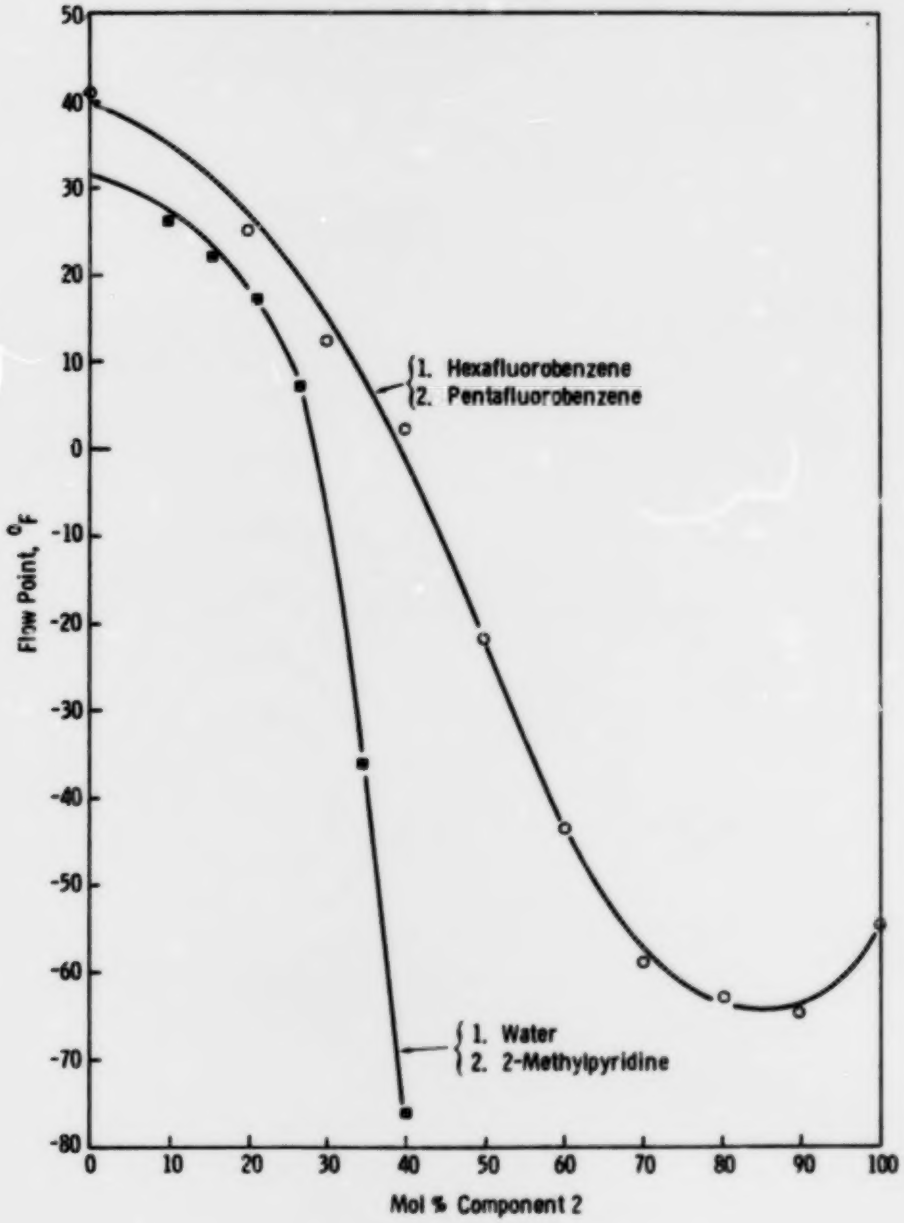

Figure 1. Flow Points of Final Candidate Mixtures

Table 2. RC-2 COMPOSITION

Component	Mol. Wgt.	Concentration Mol %	 Wgt %
water	18.0	65.0	26.4
2-methylpyridine	93.1	35.0	73.6

Note: Alternate compositions, including proportions of pyridine, 3- and 4-methylpyridine in addition to, or in lieu of, those listed, are acceptable so long as flow point requirements are met.

burn in air, it was expected that a useful diminution of flammability would occur on being mixed with water, the more so the lower the organic content.

Of the various pyridines, the 2-methyl derivative was selected for these reasons:

1. It is the most effective water freeze point depressant.
2. It has, in water solution, a thermal stability comparable to pyridine/water and somewhat higher than the other methyl pyridines (see Section 6.3).
3. Its ideal cycle efficiency (Section 6.10) is equal to or slightly higher than that of its sisters in the mol percent range of 0 to 40, the preferred low organic concentrations where the presence of water tends to reduce flammability and toxicity.
4. Its flash point, while significantly lower than those of the 3- and 4-methyl derivatives, is appreciably higher than that of pyridine itself, when compared at equal molal concentrations (Section 6.7).

The 65-35 mol ratio was selected to place the flow point just under the -40°F temperature specified as highest permissible cold-damage fluid temperature. (Refer to Figure 1). If, instead, the crystallizing point had been placed at -20°F (-29°C), the specified highest engine coldstart temperature, the 2-methylpyridine content would have been 32 rather than 35 mol percent. The presence of minor amounts of pyridine and other methyl pyridines would have only a minor effect on flow point. (Refer to Section 6.8).

Of the various fluid mixtures investigated in an attempt to radically reduce regeneration requirements (i.e. to control the shape of the dew line), only the aqueous pyridines were capable of spanning the gap in thermodynamic behavior between water -- a condensing fluid -- and such slightly superheating fluids as thiophene.

5.2 PHYSICAL PROPERTIES

Principal physical properties, measured or calculated, are recorded in Tables 3 to 12 and Figures 2 and 3 following. Contents of these presentations are:

Table	Content
3	Summary properties; molecular weights, crystallizing points, boiling points, condensing pressures, heats of vaporization, l-factor
4	Vapor pressures, RC-1 and related
5	Vapor pressures, RC-2 and related
6	Liquid densities
7	Liquid specific heats
8	Liquid kinematic viscosities
9	Liquid thermal conductivities
10	Vapor viscosities
11	Vapor thermal conductivities
12	Pseudo criticals - for extension of transport properties

Figure	
2	Vapor pressures, RC-1 and related
3	Vapor pressures, RC-2 and related

Table 3. SUMMARY PROPERTIES - FINAL CANDIDATES

Property	Final Candidate RC-1	Final Candidate RC-2
Average molecular weight	175.3	44.3
Flow point, °F	-44	-40
Normal boiling point, °F	172	200
Condensing pressure @ 220°F, psia	30	21
Heat of vaporization @ NBPT, Btu/lb	79.1	378
I-Factor at 220°F	0.72	1.38
Liquid density at 77°F, g/ml	1.549	0.985
Specific heat at 77°F, Btu/lb°F	0.290	0.668

Table 4. VAPOR PRESSURES, FINAL CANDIDATE RC-1 AND RELATED COMPOSITIONS

Composition, mol %		Vapor Pressure[1], psia				
C_6HF_5		0		(RC-1) 60	100	
C_6F_6		100		40	0	
Temperature °C	°F	Lit.[2]	Meas.	Meas.	Lit.[2]	Meas.
50	122	5.4	5.2	5.9	4.7	8.4
75	167	13.0	12.9	13.1	11.2	15.1
100	212	27.7	27.1	26.3	23.5	27.6
125	257	53.1	49.5[3]	47.1[3]	44.9	47.6[3]
150	302	93.6	91	85	79.5	80
175	347	154	152	142	132	133
200	392	239	235	221	207	210
225	437	355	355	340	310	315
250	482	506	500	480	448	460

Notes:

[1] Actually vapor-liquid equilibrium pressures, 1:1 liquid: vapor volumes (very close to bubble point pressures)

[2] Reference 1

[3] Extrapolated

Table 5. VAPOR PRESSURES, FINAL CANDIDATE RC-2 AND RELATED COMPOSITIONS

Composition / Temperature °C	°F	mol %	Vapor Pressure[1], psia				
						(RC-2)	
		Water	0	25	50	65	100
		2MP[2]	100	75	50	35	0
		Note	3	4	4	4	5
50	122		0.8	2.4	2.5	2.8	1.8
75	167		2.4	5.7	6.6	7.4	5.6
100	212		6.0	14.1	16.8	18.4	14.7
125	257		13.0	29.8	37.9	39.2	33.7
150	302		25.4	59	78	75	69
175	347		45.5	110	144	151	129
200	392		77	173	240	252	225
225	437		124	266	390	420	370
250	482		185	390	570	630	577
275	527		265	540	810	900	862
300	572		380	710	-	-	1246
325	617		440[6]	900	-	-	1749

Notes:

[1] Actually vapor-liquid equilibrium pressures, 1:1 liquid: vapor volumes (very close to bubble point pressures)

[2] 2-Methylpyridine

[3] Values below 50 psia from Reference 2, others measured

[4] Measured (by recording tensimeter)

[5] All values from Reference 3

[6] Value by extrapolation

Table 6. MEASURED LIQUID DENSITIES - FINAL CANDIDATES

Temperature		Density g/ml (at 1 atm. abs.) Final Candidate	
°C	°F	RC-1	RC-2
0	32	1.607	1.007
25	77	1.549	0.985
50	122	1.503	0.962
75	167	1.448	0.935
82	179.6	1.433	-
92	197.6	-	0.920

Method: Westphal balance

Table 7. MEASURED LIQUID SPECIFIC HEATS - FINAL CANDIDATES

Temperature		Specific Heat cal/g-C° (at 1 atm. abs. or vap. press.) Final Candidate		
°C	°F	RC-1 (Al pan)	RC-2 (Al pan)*	RC-2 (Au pan)*
25	77	0.290	0.655	0.668
30	86	0.293	0.660	0.684
40	104	0.296	0.679	0.700
50	122	0.300	0.690	0.708
60	140	0.306	0.706	0.720
70	158	0.310	0.719	0.718
80	176	0.316	0.735	0.725
90	194	0.321	0.746	0.741
100	212	0.330	0.755	0.745
110	230	-	-	0.766
120	248	-	-	0.789
130	266	-	-	0.814
140	284	-	-	0.826

Method: Perkin Elmer DSC-2 differential scanning calorimeter

* Some indication of a thermal interaction between final candidate RC-2 and the aluminum pan led to a repeat using a gold (Au) pan, which gave no indication of such interaction.

Table 8. MEASURED LIQUID KINEMATIC VISCOSITIES - FINAL CANDIDATES

Temperature		Final Candidate	
°C	°F	RC-1	RC-2
37.8	100	0.45	2.00
51.7	125	0.38	1.41
65.6	150	0.33	1.08
76.7	170	0.30	0.92

Method: ASTM D445; Cannon Manning semi-micro tubes

Table 9. MEASURED LIQUID THERMAL CONDUCTIVITIES - FINAL CANDIDATES

Temperature		Thermal Conductivity x 10^5 cal/C°-cm-sec (at 1 atm. abs.) Final Candidate	
°C	°F	RC-1	RC-2
-40	-40	26.4	-
-20	- 4	24.8	46.8
0	32	23.8	46.6
30	86	22.4	46.6
60	140	21.3	46.7
80	176	19.8	-
90	194	-	46.8

Method: Monsanto Company developed hot-wire transient measurement

Table 10. CALCULATED VAPOR VISCOSITIES AT LOW PRESSURE - FINAL CANDIDATES

Temperature °F	Absolute Viscosity of Final Candidates (Centipoise x 10^4) RC-1	RC-2
200	112	106
250	120	113
300	127	121
350	135	128
400	143	136
450	151	144
500	159	153
550	166	160
600	174	168
650	182	177
700	190	184
750	197	192
800	205	200

Table 11. CALCULATED VAPOR THERMAL CONDUCTIVITIES AT LOW PRESSURE - FINAL CANDIDATES

Temperature °F	Thermal Conductivity of Final Candidate Btu/hr-ft-°F x 10^4 RC-1	RC-2
200	62	121
250	71	131
300	79	141
350	88	153
400	97	165
450	107	178
500	116	191
550	126	205
600	136	219
650	146	233
700	156	248
750	166	263
800	176	278

Table 12. PSEUDOCRITICAL CONSTANTS FOR EXTENSION OF TRANSPORT PROPERTIES - FINAL CANDIDATES

Pseudocritical	RC-1	RC-2
Temperature, °K	508.9	615.2
Pressure, atm. abs.	37.17	127.2
Compressibility	0.2428	0.2567
Volume, cm^3/g-mol	272.8	101.9

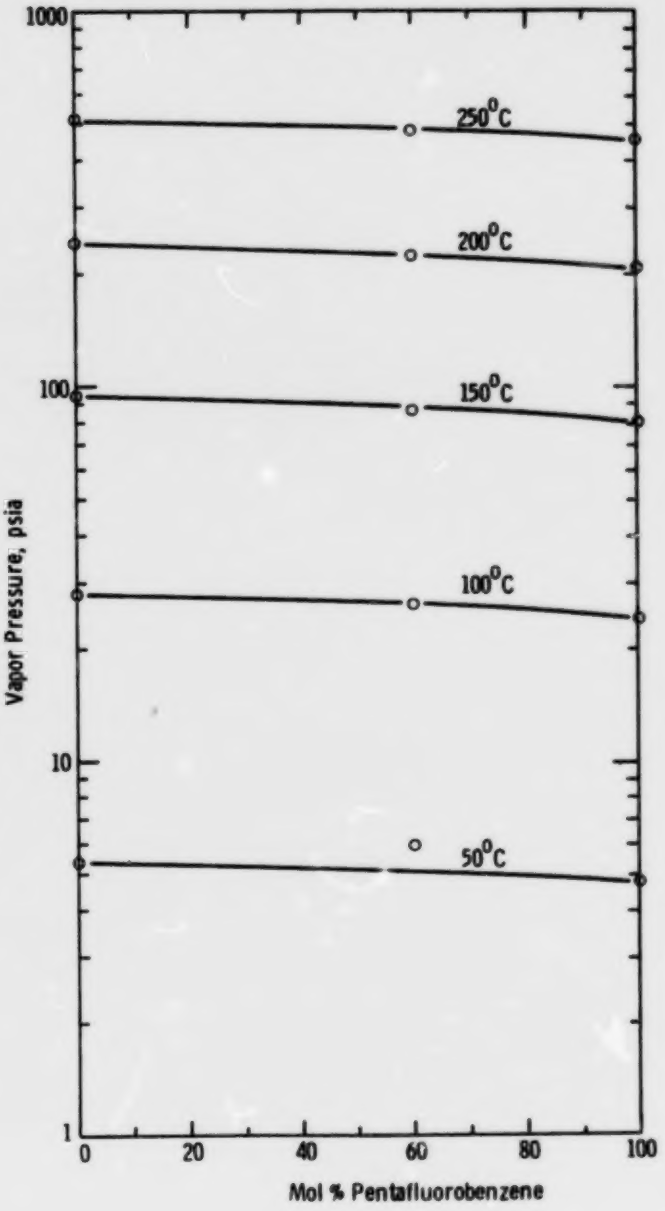

Figure 2. Vapor Pressures - RC-1 and Related

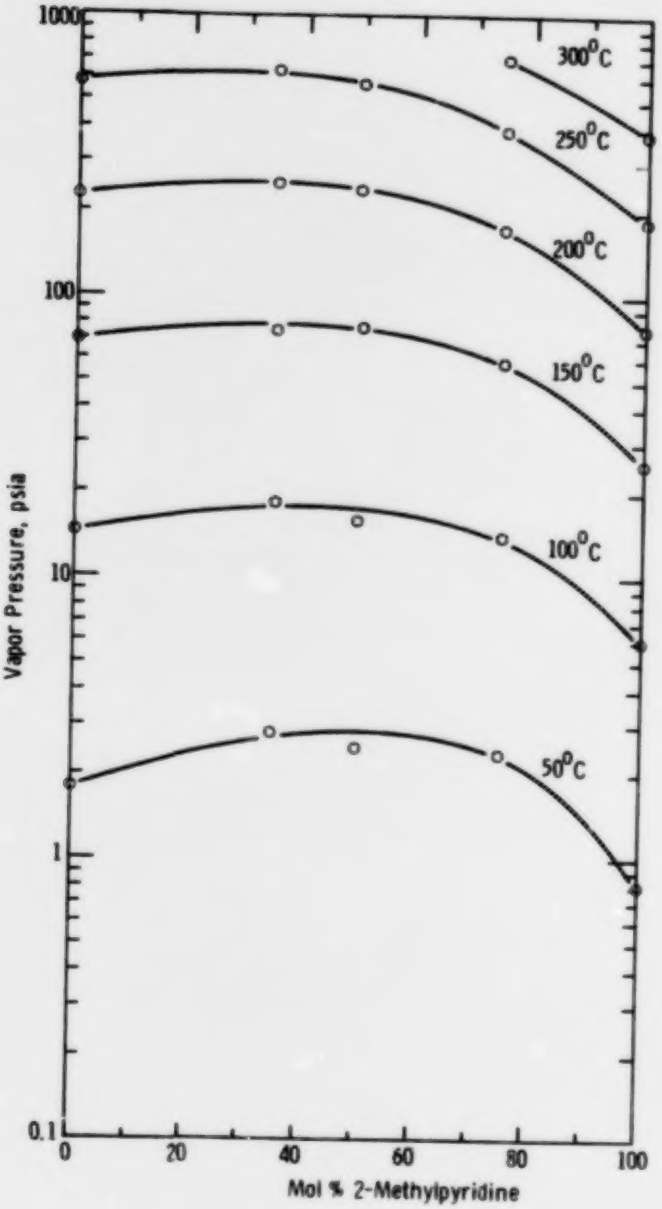

Figure 3. Vapor Pressures - RC-2 and Related

5.3 THERMODYNAMICS

Using the physical property data of Tables 13 and 14 in computer program E 1393, thermodynamic data tables were produced for each of the final candidate fluids. The resulting tables are included in Appendices B and C. Computation details are covered in Section 6.9.

Additionally, computer program TSPLOT was used to generate temperature-entropy diagrams for each candidate. These are included in Figures 4 and 5.

5.4 CYCLE CALCULATIONS

Cycle calculations for the two final candidates are presented in Table 15. Two cycles were calculated for each of the two candidates, viz:

1. Reference Ideal Cycle: an ideal Rankine cycle (clockwise rectangle on a P-S diagram) in which the isentropic expansion starts at a temperature of 712°F and ends at the bubble point pressure of the liquid at 220°F; with the added restriction that the expansion entropy be the smallest value that (a) prevents expansion into the two-phase regime, and (b) requires an expander inlet pressure no greater than 1000 psia;

2. Equivalent Real Cycle: a non-ideal (irreversible) Rankine cycle having identical working fluid conditions (referred to the above cycle) at the two "opposite" cycle corners, i.e. at the vapor generator exit and the condenser exit, but otherwise characterized by the following efficiencies and pressure drops:

Efficiencies (fluid indicated)	
expander	75%
pump	75%
Pressure losses	
vapor side, regenerator	0.09 P_4
condenser	0.14 P_4
liquid side, regenerator	0.05 P_1
vapor generator	0.10 P_1

where P_1 and P_4 are the absolute pressures at vapor generator and condenser exits respectively; with the added restriction that the regenerator UAk product (or $Q/\Delta T_{\text{log mean}}$) be fixed at 125 Btu/HP-hr-°F, the "largest" regenerator believed acceptable in a turbine driven automobile according to Criterion 7, Section 6.1.

Additional explanatory notes keyed to Table 15 are:

Table 13. PHYSICAL PROPERTY DATA USED IN THERMODYNAMIC TABLE GENERATION FOR FINAL CANDIDATE RC-1

	C_6F_5H	C_6F_6
Molecular Wt.	168.067	186.057
Critical Temp. (°K)	503.7	516.72
Critical Pressure (atm)	24.7	32.61
Critical Compressibility	0.2181	0.2799
Critical Volume (cm^3/g-mol)	356	364
Heat Capacity, ideal gas ($Cp = a + bT + cT^2 + dT^3$) Btu/lb mol-°F or cal/g-mol-°C T in °K		
a	-1.2077	0.2994
b	0.112202	0.111666
c	-7.108×10^{-5}	-7.05×10^{-5}
d	1.611×10^{-8}	1.575×10^{-8}
Vapor Pressure [$\ln P^\circ = A + B/(T + C)$] P° in atm, T in °K		
A	11.72714	11.54669
B	-4535.12	-4369.7
C	28.57	25.287
Heat of Vaporization (cal/g-mol)	7729	7651
at T (°K)	358.15	353.15
Liquid Density (g/cm^3)	1.522	1.613
at T (°K)	298.15	298.15

Van Laar Constants = 0 for this pair; mixture assumed an ideal solution.

Table 14. PHYSICAL PROPERTY DATA USED IN THERMODYNAMIC TABLE GENERATION FOR FINAL CANDIDATE RC-2

		2-Methylpyridine (Component 1)	Water (Component 2)
Molecular Wt.		93.129	18.016
Critical Temp. (°K)		621.1	647.3
Critical Pressure (atm)		45.4	218.2
Critical Compressibility		0.297	0.230
Critical Volume (cm^3/g mole)		333.2	56
Heat Capacity, ideal gas ($Cp = a + bT + cT^2 + dT^3$) Btu/lb mole-°F or cal/g mole-°C T in °K			
	a	-4.1626	7.136
	b	0.116616	0.00264
	c	-6.68199×10^{-5}	4.59×10^{-8}
	d	1.301498×10^{-8}	0
Vapor Pressure [$\ln P^\circ = A + B/(T + C)$] P° in atm, T in °K			
	A	10.429	12.144
	B	-3957	4203.9
	C	-22.68	-26.75
Heat of Vaporization			
(cal/g mole)		8654	9717
at T (°K)		402.55	373.15
Liquid Density			
(g/cm^3)		0.9497	1.
at T (°K)		288.15	277.15

Van Laar Constants (T in °K):

$A_{12} = 3.9654 + 792.79/T - 0.0089793\ T$

$A_{21} = 11.984 - 1997.1/T - 0.0146616\ T$

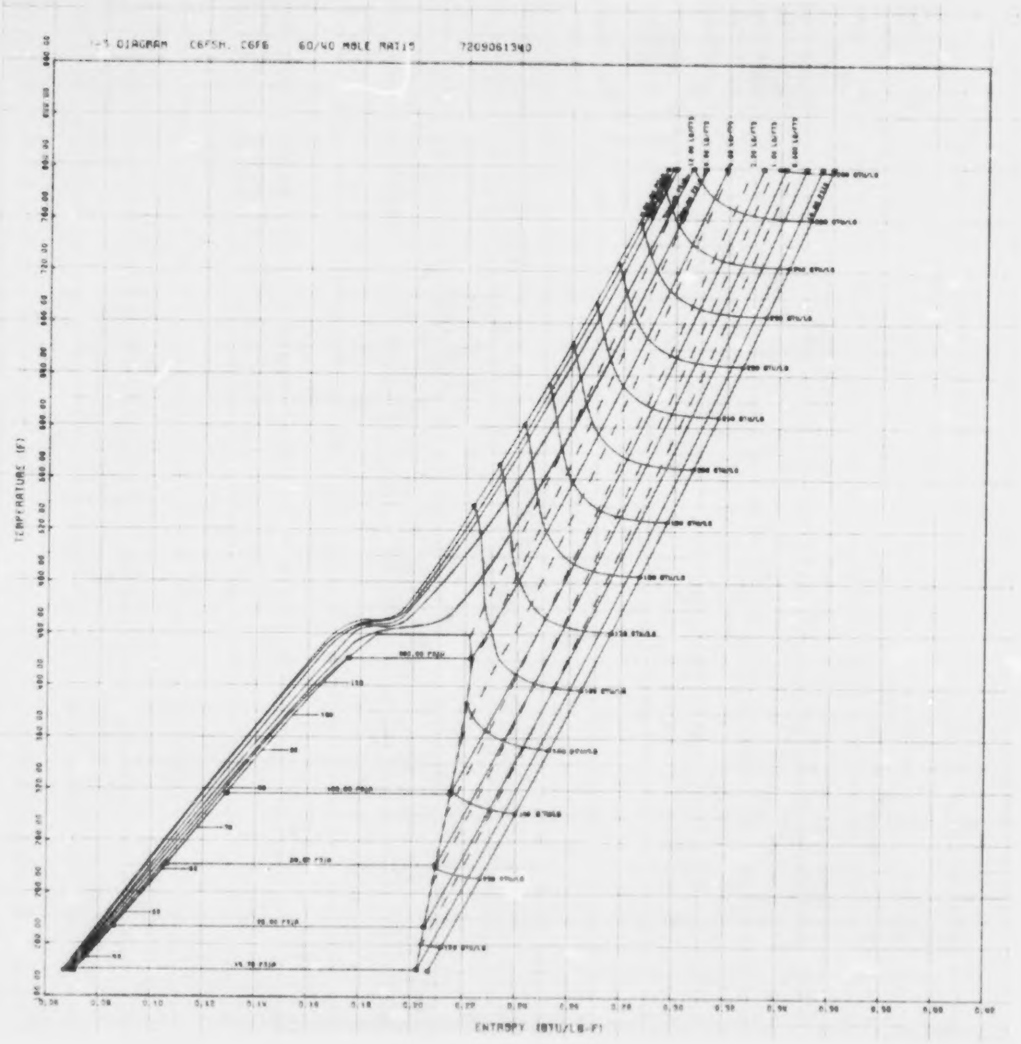

Figure 4. Temperature-Entropy Diagram - RC-1

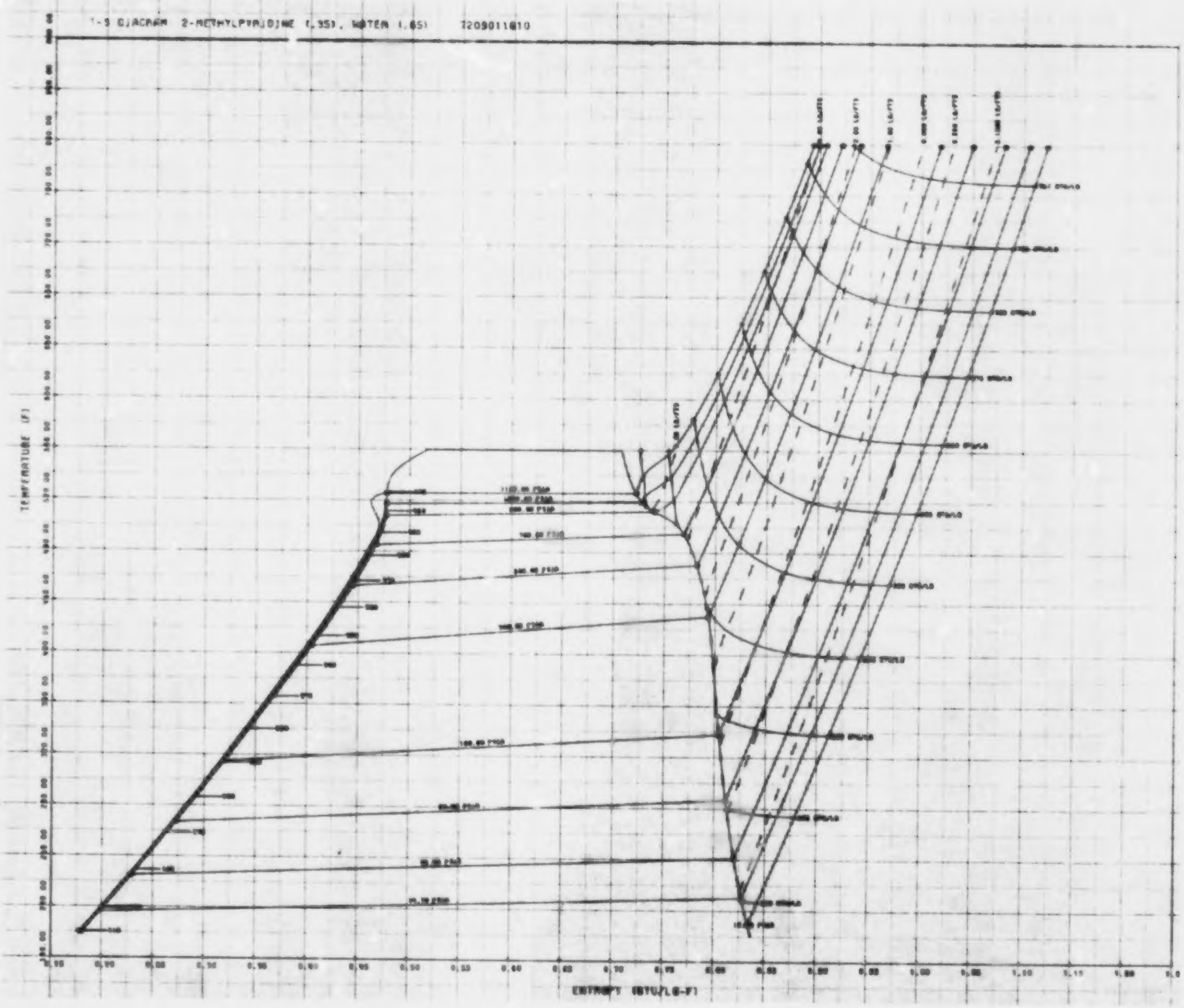

Figure 5. Temperature-Entropy Diagram - RC-2

Table 15. RANKINE CYCLE SUMMARIES, FINAL CANDIDATES

	RC-1		RC-2	
Cycle	Ideal[1]	Real[2]	Ideal[1]	Real[2]
Efficiencies, %				
Cycle	30.00	20.95	28.8	22.15
% of Carnot	71.45	49.88	68.57	52.74
Cycle, 0% Rgn.	20.54	13.35	26.84	18.57
100% Rgn.	30.69	22.07	28.8	22.23
Carnot	42.00	42.00	42.00	42.00
Temperatures, Max, °F	712	712	712	712
Min, °F	220	220	220	220
Pressures, Max, psia	1000	1150	1000	1150
Min, psia	27.31	27.31	22.94	22.94
Per 100 Cycle HP:				
Fluid Rate, lb/hr	7470	11,521	1756	2521
Eng. Exh., cfm	259.1	340.0	233.4	310.1
Pump In, gpm	12.24	18.81	3.93	5.66
Engine HP, gross	107.34	116.84	102.43	105.04
Pump HP	7.34	16.84	2.43	5.04
Heat Flows				
Heater, kBtu/hr	848.4	1214.1	883.3	1148.9
Regen, kBtu/hr	390.5	691.7	64.8	212.8
Conden, kBtu/hr	408.5	949.5	628.8	890.1
Without Regen				
Heater, kBtu/hr	1238.8	1906.5	948.1	1361.7
Conden, kBtu/hr	799.0	1641.2	693.6	1102.9
Engine: % Effic =	100	75.0	100	75
Pressure Ratio	36.62	29.77	43.59	35.44
Density Ratio	44.55	37.91	35.60	32.94
Isentropic (3)	44.55	15.4	35.60	12.06
Exhaust Qual, %	176.5	189.7	107.5	118.1
Delta -H, Btu/lb	36.57	25.81	148.5	106.0
Isentropic	36.57	15.29	148.5	141.4
Nozzles, Coef =	1.00	0.95	1.00	0.95
V spout, fps	1353.0	1262.4	2726	2587
Mach No. spout	2.48	2.40	2.95	2.74
A throat (4)	0.052	0.118	0.066	0.049
Regen: % Effect =	95.3	91.8	100	98.4
Q, kBtu/CHP-hr	390.5	691.7	64.8	212.8
UA, kBtu/CHP-hr-°F	11.98	12.5	∞	12.5
Delta T_1 LM, °F	32.6	55.6	0	23.0
NTU, OG	7.47	4.92	∞	7.36
I-Factor, 220°F	0.719	0.719	1.379	1.379
Pump: % Eff.	100	75	100	75
Pressure Ratio	36.62	42.11	43.59	50.13

Notes covered in text.

3. The isentropic density ratio is calculated over a hypothetical isentropic expansion from engine inlet condition to an enthalpy equal to real cycle engine exhaust enthalpy; it is, then, a good approximation of the minimum permissable expansion ratio [(displacement + clearance volume)/(clearance volume)] to be provided in the design of a reciprocating expander of matching performance. Refer to Criterion 9 of Section 6.1.

4. The combined turbine nozzle throat cross sectional area required per 100 cycle HP assuming choked flow (cycle HP is net fluid-indicated HP, expander less pump). Additional computation details are given in Section 6.10.

A comparison of the data of Table 15 with the fluid selection criteria of Section 6.1 permits several interesting observations. Candidate RC-2 fails the 30% ideal cycle efficiency dictum of Criterion 6, yet it has a higher real cycle efficiency than does RC-1 by over two percentage points. It therefore appears that RC-2 should not be disqualified solely on the basis of its ideal cycle efficiency of 28.8%. While RC-1 shows ideal and real cycle efficiencies of 30 and 21%, it may be noted that RC-1 was found to be more thermally stable at 720°F than RC-2 so it actually could be pushed higher in temperature to where it would show even more advantageously in efficiency than RC-2. By Criteria 8 and 9, both candidates qualify for both reciprocating and turbine expanders.

The assumption of a "smaller" regenerator than the UAk = 125 Btu/HP-hr-°F of the Table 15 real cycle calculations, as to account for the lesser available compartment space with a reciprocating plant, would lower the real cycle efficiencies on both candidates, and would therefore make fluid RC-2 look more attractive in a reciprocating plant competing with a turbine engine utilizing RC-1.

Table 15 also reveals a significant difference in working fluid circulation rates compared at equal cycle power levels. About four times as much RC-1 needs to be circulated as RC-2 (by weight). One consequence is the need for a three times as powerful pump with RC-1. Another consequence is the need for larger conduits and components with RC-1 to avoid the higher pressure losses normally accompanying higher mass flow rates. These disadvantages of the RC-1 fluid are traceable to the lower available energy of expansion per unit mass associated with higher molecular weight fluids. Attempts were made to quantize molecular weight as a selection criterion despite a lack of contractual restrictions. The attempts failed because of the ill-defined and complex ways molecular weight enters into system goodness.

A fact not apparent in Table 15 is that the RC-1 cycles are supercritical, whereas the RC-2 cycles are subcritical. Again, no restrictions were imposed in this case. It appears that each type of cycle has its supporters and detractors, and no judgment is offered here on which may be superior.

5.5 STABILITY/COMPATIBILITY TESTS

5.5.1 Dynamic Loop Testing

Final candidate working fluids were subjected to extended loop testing under conditions approximating prototype. The purpose of dynamic loop testing was to demonstrate fluid stability, materials compatibility and energy exchanges in a real flowing system.

5.5.1.1 Description of Loops - Two identical dynamic loops were constructed. Figure 6 is the loop schematic showing the arrangement of the various components. Table 16 gives component details. An overall view of one of the loops appears in Figure 7. Procedures followed in conducting the tests are given in Appendix D.

Each heater coil, as noted in Table 16, was made by bending a 100-inch length of 0.25 inch OD SAE 4130 steel tubing into the trombone shape shown in Figure 8. The tubing was used as received, with no internal pretreatment other than the solvent cleaning procedures of Appendix D. The internal surface of the new tubing was found to have a smooth dull black oxide finish. A photomicrograph appears in Figure 9a.

In use, the heater coil was heated by Dowtherm A condensing on the outer surface of the tubing. This heating mode was provided to eliminate all question of the presence of hot spots along the coil. Hot spots are difficult to control, especially when electrical heat is used to boil a fluid to dryness at a pressure below its critical pressure.

Condenser coils, as typified in Figure 10, were fabricated by wrapping the 0.25 inch OD 3003 aluminum tubing around a mandrel. The tubing was used as received. Solvent rinsing (as described in Appendix D) was the only internal treatment employed. Figure 9b shows the initial surface. To the eye this surface appeared as a gray oxide finish with very distinct drawing marks.

During testing, the condenser coil was immersed in hot flowing tap water. In order to prevent electrolytic corrosion of the outer surface of the aluminum, a sacrificial anode system was employed. The flowing water (the electrolyte) was confined in a plastic beaker. A 1.5-volt dry cell was connected to the condenser coil (the cathode) and to the sacrificial anode (a one inch

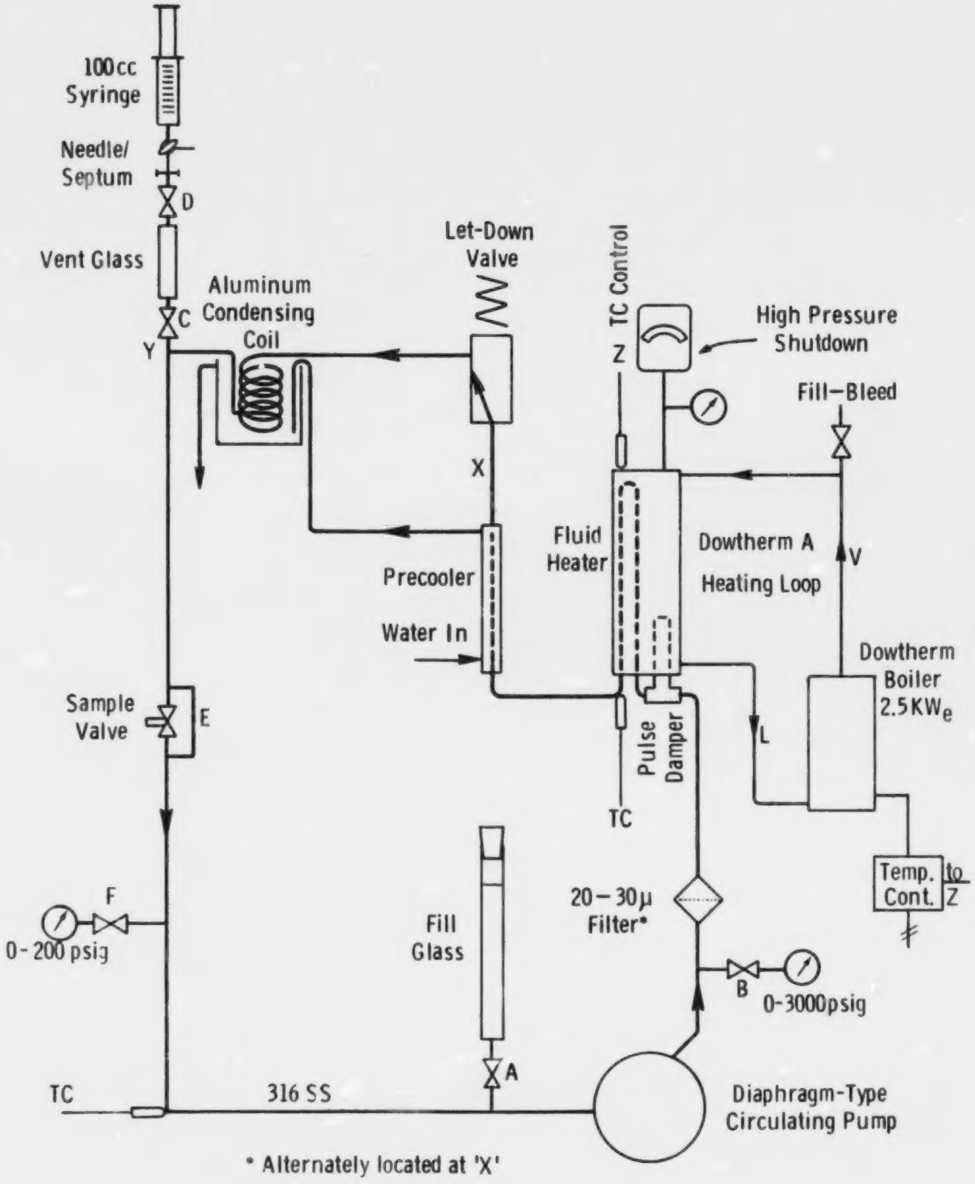

Figure 6. Dynamic Loop Schematic

Table 16. DYNAMIC LOOP PARTICULARS

Item	Description
Pump	Lapp CPS-1, variable positive displacement, SS diaphragm and wetted parts, PTFE seals.
Filter	Hoke #6311G4S, 20-30 micron SS frit element
Pulse Damper	7 in. length, 1/2 in OD, SS tube, vapor cushion
Heater Coil	SAE 4130 steel, 0.25 in. OD x 0.035 in. wall x 100 in. long, formed into 4-pass hairpin coil
Precooler	7 in. length* of water jacket around run of 0.25 in. OD x 0.035 in. wall SS tubing
Let-down Valve	Republic #644XB-9-4-2, 5/16" D. ball subs. for poppet
Condensing Coil	3003 aluminum, 0.25 in. OD x 0.035 in. wall x 60 in. long, formed into 7-turn helical coil.
Sample Valve	Hoke #7115G4Y with Swagelok #100-R-2-316, fitted with a septum, silver soldered in the side at ball centerline.
Loop Tubing	316 SS, 0.25 in OD x 0.035 in. wall (except heater and condenser coils above)
Loop Fittings	316 SS Swagelok, 303 & 316 SS Hoke valves, SS ferrules
Dowtherm A Loop	Boiler: 2.0 in. OD x 21 in. long, 10 x 250 W cuff heaters Exchanger: 2.0 in. OD x 26 in. long Vapor tubing: 0.5 in. OD, 316 SS Liquid tubing: 0.375 in. OD, 316 SS Insulation: 1" silicate pipe cover, 1" ceramic blanket
Temp. Controller	Galvanometer type, on/off mode, I/C couple
Temp. Recorder	Brown multi-point type, I/C thermocouples
Pressure Gauges	Steel bourdon tube type, 0-200 and 0-3000 psig, with zero-pressure pointer stops removed.

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*See text for exception, second RC-2 test

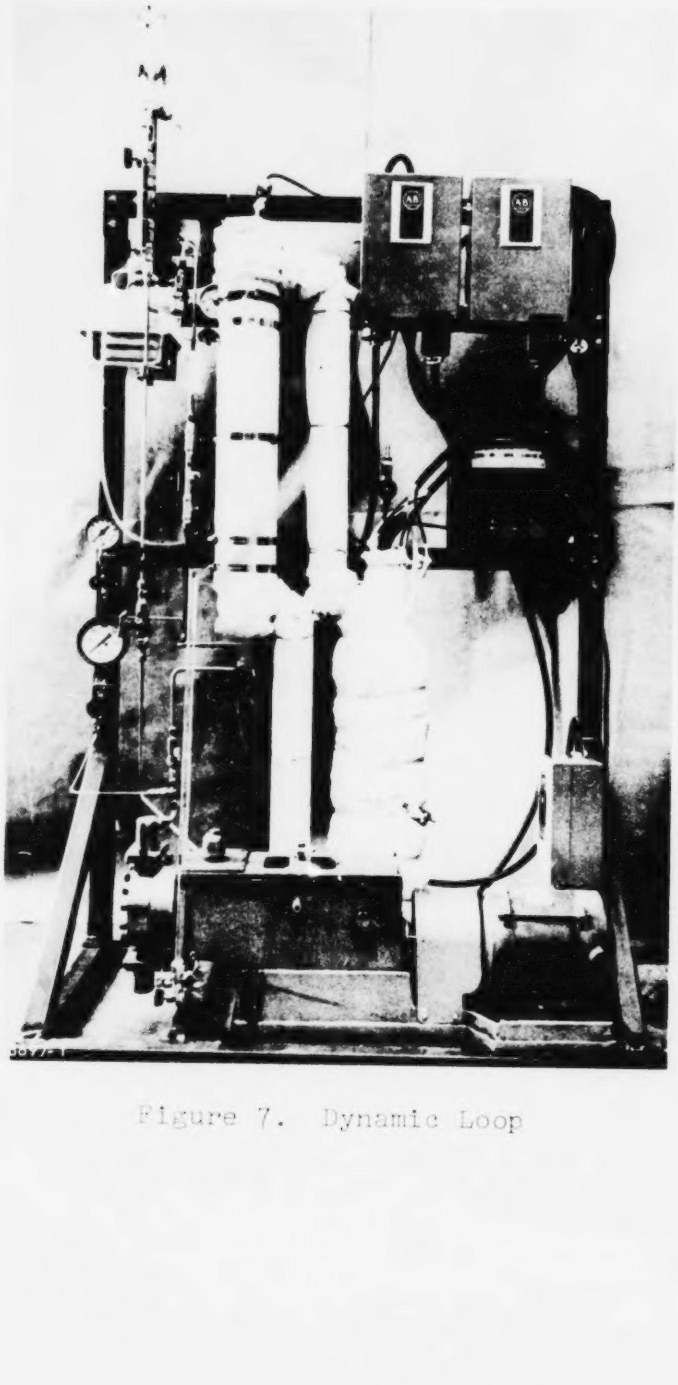


Figure 7. Dynamic Loop

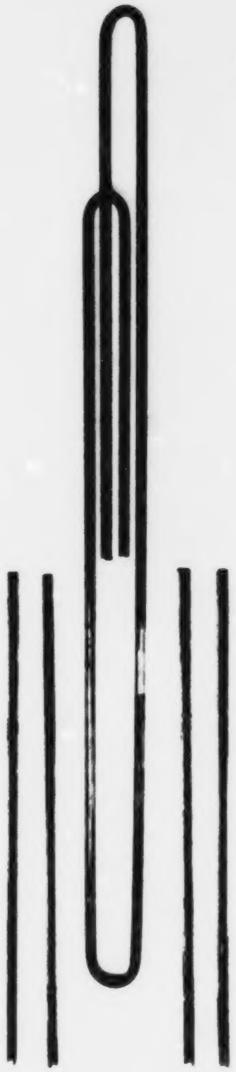
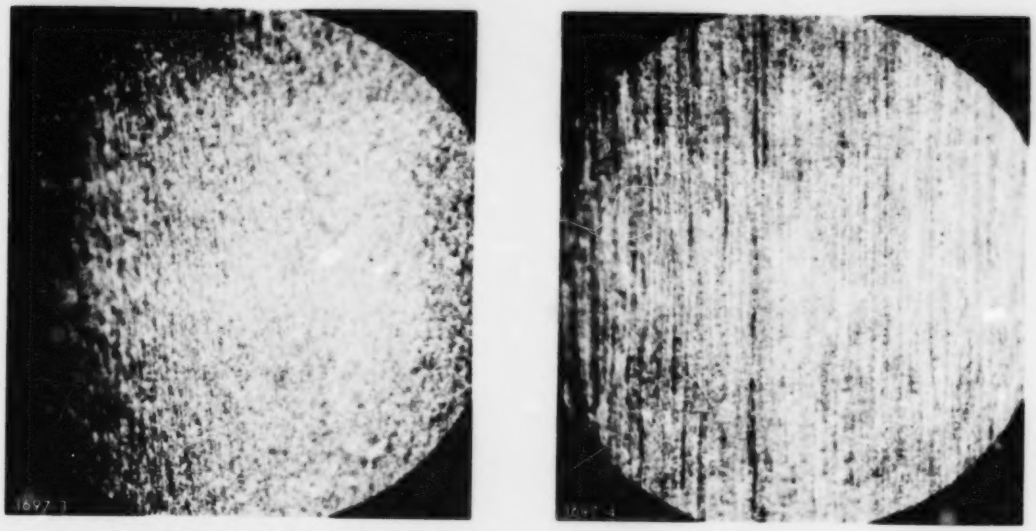


Figure 8. Heater Coil - Ends Cut and Sectioned Lengthwise for Examination



9a. Steel (Heater)

9b. Aluminum (Condenser)

Figure 9. Photomicrographs of Heat Exchanger Surfaces before Use (27x)

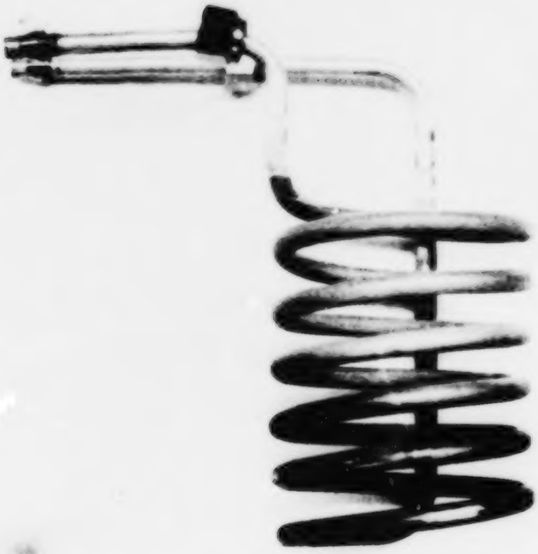


Figure 10. Aluminum Condenser Coil

square of sheet magnesium) suspended at the center of the coil. Every 2-3 days the deteriorated anode was replaced. This system effectively prevented external corrosion, but did not, of course, prevent calcium/magnesium scaling.

This design was based upon a similar dynamic loop constructed and operated at Aerojet Liquid Rocket Company, Sacramento, in 1971-2. Features common to the two designs include the tubing materials and sizes and general component arrangement. The major features of the present loop not borrowed from the Aerojet design are:

- heating of fluid by condensing Dowtherm A vapor (vs. electrical resistance windings)
- positive displacement pumping

5.5.1.2 Test Description - Conditions of testing were as listed in Table 17.

Table 17. DYNAMIC LOOP TEST CONDITIONS

Controlled Values	
pump discharge pressure	1000 psig
heater exit bulk temperature	720°F
pump suction pressure	15-30 psig
fluid flow rate	see text
Typical Values	
pump suction temperature	100-110°F
cooling water in temperature	40-60°F
Dowtherm A condensing pressure	120-160 psig
Dowtherm A condensing temp.	735-770°F
system volume (measured)	190-200 cc
heater tube volume (calc.)	41.6 cc
Elastomer Seals	
pump diaphragm, check valves	PTFE
filter	PTFE
let-down and sample valve O-rings	see text
sample valve ball seals	Kel-F or PTFE
all other valves	Kel-F or PTFE

The detailed test procedure is presented in Appendix D. A test "pass" is 1000 hours of successful operation with no operational problems attributable to fluid instability, incompatibility or corrosion.

5.5.1.3 RC-1 Test Results - The test of RC-1 started 18 October 1972 under the conditions and with the results listed in Table 18. Early in the test a very slow but persistent leak developed. The source of leakage was eventually traced to the end fittings on the aluminum condenser coil (through the use of a sensitive thermal conductivity vapor detector).

At 498 hours the test was interrupted long enough to remove the stainless steel ferrules originally installed in the end fittings and replace them with aluminum ferrules. As this cured the chronic leakage problem, it was subsequently adopted as standard. A mismatch in elasticity or thermal expansion coefficient between the aluminum and stainless steel is believed to have been the cause of the leakage.

In all other respects the test was nominal. The outcome was, therefore, rated "pass".

Table 18. LOOP TEST SUMMARY, RC-1

Test & fluid	RC-1
Outcome	pass
Dates	18 Oct. to 6 Dec. 1972
Duration (at temp.)	1172 hr
Termination Reason	time expired
Pumping rate	110 ccpm
O-ring elastomer	Viton (Parker 747-7)
Zero time exceptions*	
Forerun	-
Condenser Ferrules	-
Letdown valve	-
Filter	-
Gas measurement	-
Vent glass tee	-
Fluid additions	16 cc (in first 1000 hr)
Vented gas	
Cumulative RTP volume	0 cc
Over span of	840 hr
For average rate of	0.0 ccph
Filter changes	none

---

*Exceptions to the data of Table 16 or the procedures of Appendix D.

Microscopic examination of internal heat exchange surfaces, exposed by slicing sections from each end of each coil, produced these observations:

1. Heater inlet (cold) end (Figure 11a); smooth black oxide finish as in new tubing, but with a band of brown deposit at entry end presumed to be ordinary rust, Fe_2O_3.

2. Heater outlet (hot) end (Figure 11b); smooth black oxide finish as in new tube but with off-black striated patches visible - no loose deposits.

3. Condenser inlet (hot) end (Figure 11c); same appearance as new tubing.

4. Condenser outlet (cold) end (Figure 11d); same appearance as new tubing.

Fluid removed from the loop at 1002 hours appeared water white. Analyses of the new and used fluid by gas-liquid chromatography and mass spectroscopy permits the conclusion that only the subtlest of chemical changes occurred. The major impurities present in the new and used fluid and their approximate concentrations were as follows:

	Parts per Million	
Contaminant	New	Used
fluorinated aliphatics	410*	710
chloropentafluorobenzene	4200**	3100
unknown, MW - 258	0	820

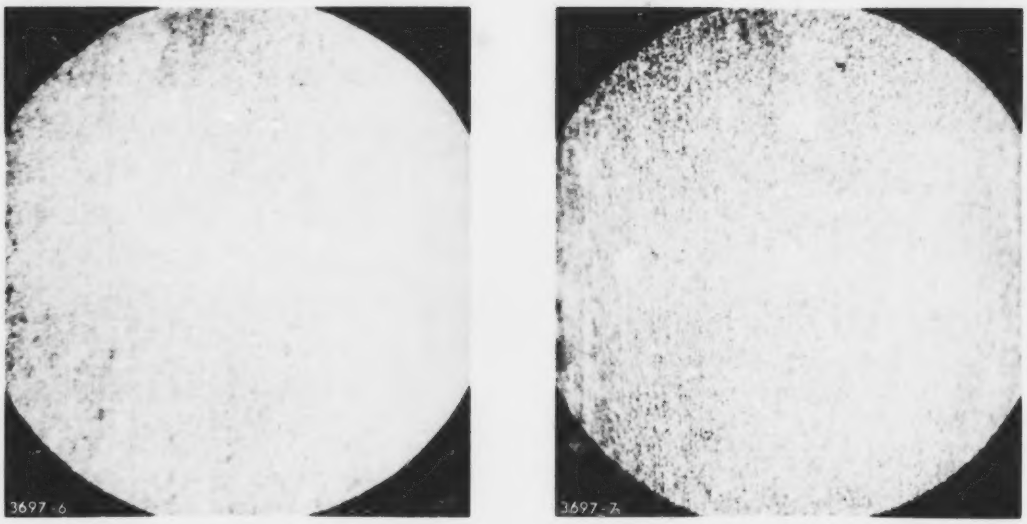
---

*primarily from the hexafluorobenzene sample

**primarily from the pentafluorobenzene sample

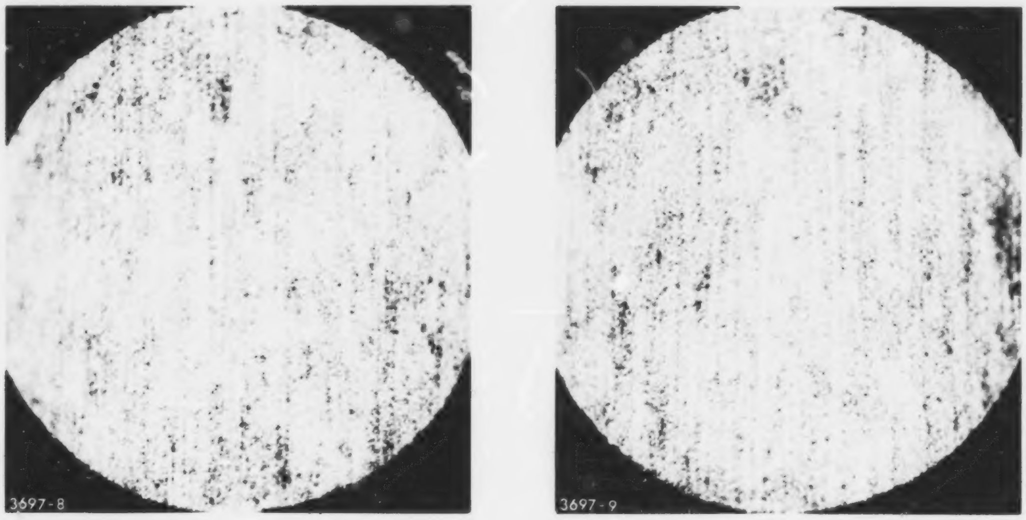
These data suggest that the main decomposition mechanism was one that converted the main initial contaminant, chloropentafluorobenzene, into a higher molecular weight compound and one or several lower boiling fluoroaliphatics. This is plausible in light of the finding reported elsewhere that chlorinated compounds are simply not as stable as fluorinated compounds. In any event, the extent of decomposition was well below the levels of the contaminants alone in the starting fluid.

5.5.1.4 First RC-2 Run Test Results - The first RC-2 test, summarized in Table 19, revealed several flaws in the original loop design, one of which was responsible for the early abortion of the test.



11a. Inlet (Cold) End 11b. Outlet (Hot) End

Steel Heater Coil



11c. Inlet (Hot) End 11d. Outlet (Cold) End

Aluminum Condenser Coil

Figure 11. Photomicrographs of Heat Exchanger Surfaces after RC-1 Test (27x)

Table 19. LOOP TEST SUMMARY, FIRST RC-2

Test & fluid	RC-2 (first)
Outcome	Fail - incompatibility
Dates	6 to 23 October, 1972
Duration (at temp.)	400 hr
Termination Reason	fluid loss, flow loss
Pumping rate	approx. 56 ccpm (estimated)
O-ring elastomer	EPR rubber (Parker E515-8)
Zero-time exceptions*	
Forerun	-
Condenser ferrules	stainless steel
Letdown valve	unmodified (as received)
Filter	-
Gas measurement	not provided (until 287 hr)
Gauge glass tee	-
Fluid additions	15 cc
Vented gas	
Cumulative RTP volume	450 cc (287 to 400 hr)
in span of	113 hr
for average rate	4.0 ccph
Filter changes	One (305 hr)

---

*Exceptions to Table 16 or Appendix D.

During the first week of the test, difficulty was experienced in maintaining a constant 1000 psig pump discharge pressure, and many adjustments of the let-down valve bonnet were needed. Some slow leakage was experienced, mainly through the O-ring seal on the bonnet. In addition, no diminution in the amount of vent gas was noted after the first few days operation.

At the 305-hour mark, the test was interrupted to repair leaks in the sample and let-down valves. The sample valve was replaced on account of galled and leaky threads and a new EPR O-ring was installed in the let-down valve after resurfacing the valve seat and replacing the original poppet valve with a 5/16 in. D. steel ball. Loose black deposits found in the porting areas of the valve in disassembly were collected and analyzed. Similar material was found on the filter element (which was replaced) and in fluid drained from the heater coil.

A 100-cc syringe with 3-way valve was mounted above the vent glass to permit measurement of vent gas volumes. The arrangement is shown in Figure 12. The original fluid drained from the system was replaced, and 15 additional cc of new fluid were needed to make up for disassembly losses. The test was then restarted.

Operation continued fairly smoothly for the next 50 hours, but then erratic high pressure control was again experienced. At 400 hours the test was aborted upon discovering loss of fluid circulation and excessive fluid leakage through the fitting at the condenser coil inlet.

During the last 113 hours of this test, some 450 cc of vent gas were collected. The major constituent of this gas was found by mass spectroscopy to be hydrogen. The black deposits mentioned above were observed to be fully magnetic. By x-ray diffraction it was discovered that a major (if not sole) ingredient of this material was Fe_3O_4

The test was rated a "fail". Erratic control of pump discharge pressure is ascribed to black iron oxide deposits in the let-down valve preventing normal valve seating and free valve movement.

Microscopic examination of internal heat exchange surfaces, exposed by slicing sections from each end of each coil, produced these observations.

1. Heater inlet (cold) end (Figure 13a); smooth black oxide finish as in new tubing, but with an inch wide band of brown deposit at entry end presumed to be ordinary rust; one very striking corrosion pit was noted in this portion of the coil (as shown in Figure 14; no others were spotted, so the one must be considered atypical.

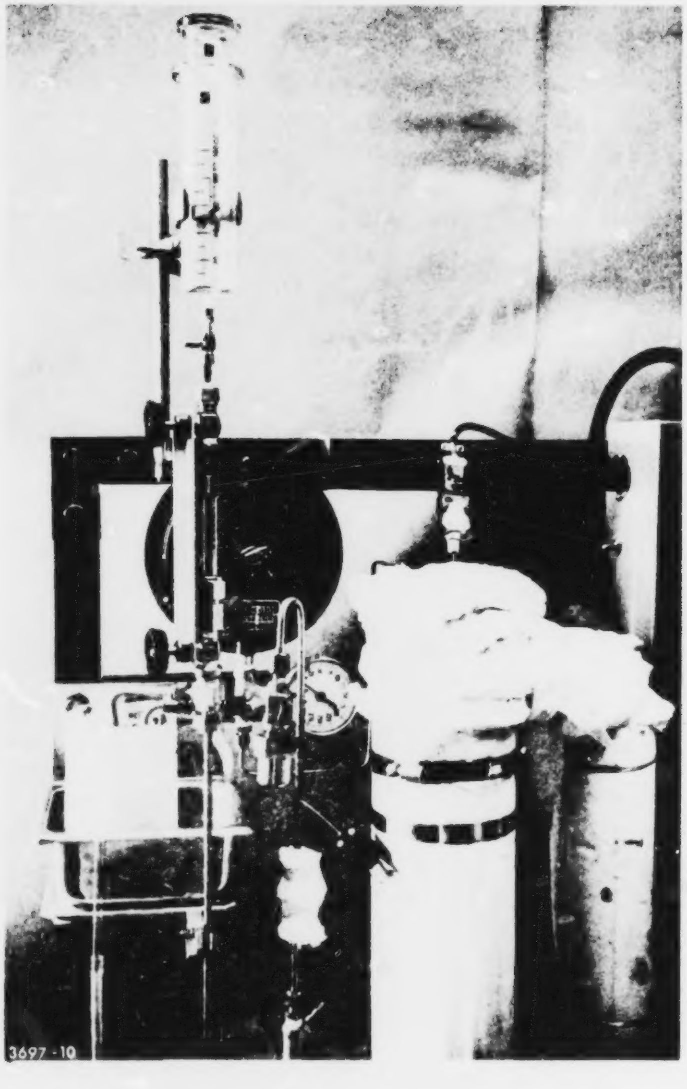
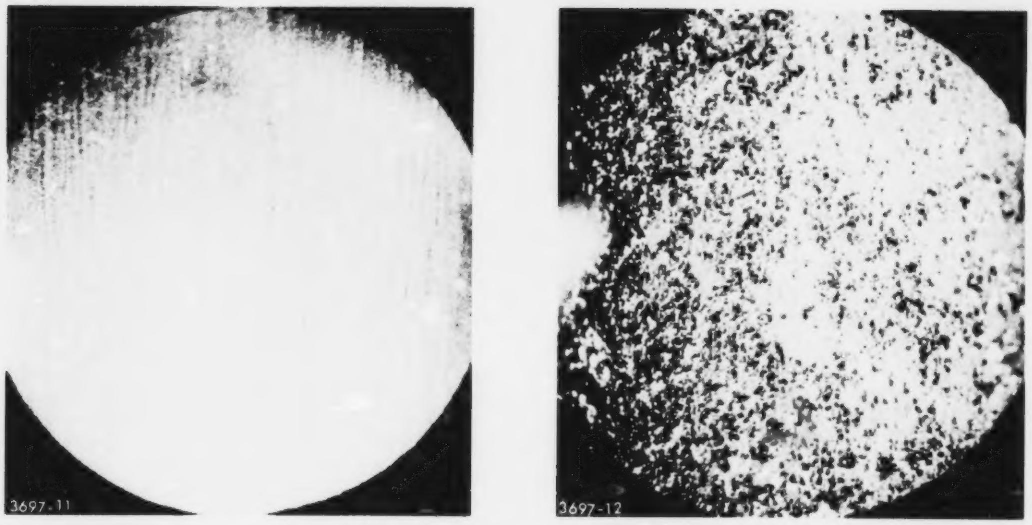
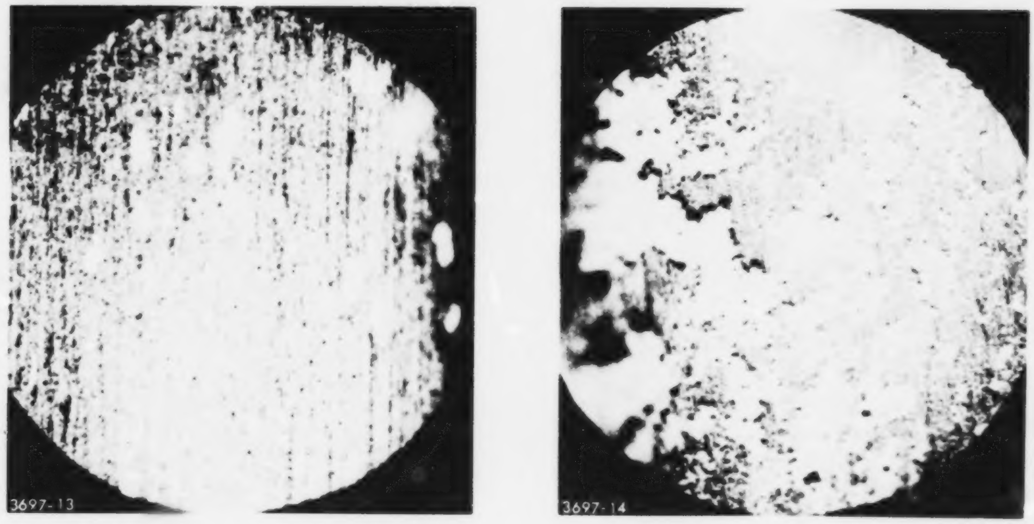


Figure 12. Vent Gas Syringe Arrangement



13a. Inlet (Cold) End 13b. Outlet (Hot) End

Steel Heater Coil



13c. Inlet (Hot) End 13d. Outlet (Cold) End

Aluminum Condenser Coil

Figure 13. Photomicrographs of Heat Exchanger Surfaces after First RC-2 Test (27x)

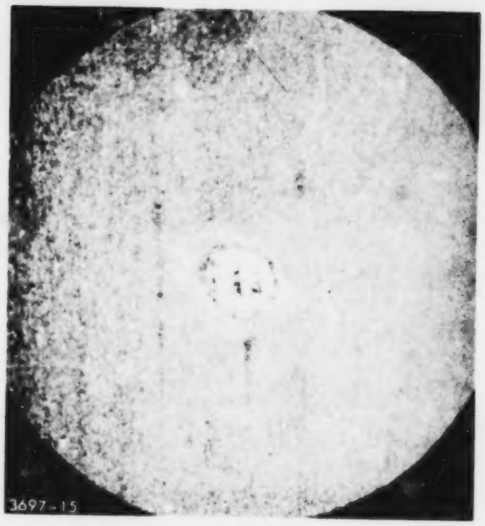


Figure 14. Photomicrograph of Pit in Heater Tube after First RC-2 Test (27x)

2. Heater outlet (hot) end (Figure 13b); smooth black oxide finish as in new tubing, but overlaid with patchy clusters of loosely-adherent shiny black crystals of Fe_3O_4

3. Condenser inlet (hot) end (Figure 13c); brown deposit estimated half mil thick covering surface everywhere but in isolated silvery patches; scrapings are magnetic and are presumed to be Fe_3O_4 crystals embedded in a whitish inorganic matrix.

4. Condenser outlet (cold) end (Figure 13d); same as condenser inlet except deposit is thinner, smoother and possesses fewer gaps.

Evidence points clearly to a corrosion reaction between water and iron,

$$3Fe + 4H_2O \longrightarrow Fe_3O_4 + 4H_2,$$

in the steel heater tube, which resulted in the copious release of gas and formation of Fe_3O_4 particles. The former required frequent purging, while the latter ultimately caused malfunctions in the letdown valve. Both of these constitute evidence of incompatibility.

5.5.1.5 Second RC-2 Loop Test Results - The first RC-2 loop test was ended prematurely by the steady formation of magnetic iron oxide and hydrogen, both of which interfered with nominal operation. Continuous reaction of water with iron, however, is not the inevitable result of contacting water with steel at elevated temperature. Many years of experience with steel-tubed boilers and superheaters in power plants proves this. On startup of new steel tube boilers, it is common to find significant amounts of hydrogen in the steam for the first day or so of operation, but the formation rate then declines to practically zero for the rest of the useful life of the tubing. This self-passivation phenomenon is thought (ref. 4) to depend on the formation of a chemically-resistant film of oxide and possibly of hydrogen on the metal surface. Hydrogen film passivation is called polarization.

Failure of the steel heater tube to self-passivate could be linked to:

a. improper surface treatment
b. incorrect choice of steel
c. presence in the water of the 2-methylpyridine
d. combination of above

A second loop test of RC-2 was scheduled to try to resolve this issue. Attempts to purchase 0.25 in. OD steel tubing to ASTM specifications A210 or A213 Grade T11 (typical steels for boiler and superheater tubing) failed. Stainless steel could have been chosen and likely would have solved the corrosion problem, but stainless steel appears not to satisfy the criterion of a "low cost" metal of system construction. Other low cost steels which might have been chosen were not, since there was no reason to believe they would be better than the SAE 4130.

The decision was therefore made to retain the SAE 4130 steel for the heater tube. It was further decided to attempt to prepassivate this tubing in-situ by "running in" on pure water. If the steel could be prepassivated with water, it was reasoned, there would then be hope that it would remain passive to the RC-2 fluid. This was the rationale behind the second RC-2 loop test.

Several changes in the loop hardware were made prior to starting to ease problems encountered in the first RC-2 test. The most important of these was the relocation of the filter (to point "X" in Figure 6) to keep solids from interfering with the let-down valve. To accommodate this change, it was also necessary to enlarge the precooler (to 12 in. length) so as to drop the filter body temperature below the 500°F limitation of its PTFE seal gasket. Another change was the replacement of the vapor-separating tee at point "Y" of Figure 6 to secure more positive liquid-vapor separation. This was done because of a suspicion that gas bubbles had been accumulating in pump suction regions and had been contributing to flow stoppages.

The change consisted of the substitution of a 1/4 inch IPS stainless steel pipe tee for the original tubing tee. The 1/4-inch OD inlet tube was allowed to project into the tee body through the lateral opening. Its end was sectioned laterally for about one-half inch to afford an easy upward escape of bubbles. Although this change undoubtedly improved the gas-liquid separation efficiency of the vent tee, it brought about no noticeable changes in loop operation or behavior.

On 5 December 1972 the loop was filled with distilled water and put into operation under standard conditions. After the first four days of running no bubbles appeared at the sight glass. This was interpreted as successful attainment of the passive condition. This forerun was ended after 285 hours hot operation.

The water was drained and blown from the loop and new RC-2 charged on 18 December 1972. The second test of this fluid then commenced under the conditions and with the results of Table 20. The run proceeded smoothly until 167 hours when it was necessary to shut down to clean scale from the outside of the condenser coil and clean up a resultant water spill. During this shutdown inspection of the filter element showed it to be heavily clogged with black oxide particles, so it was replaced.

At 238 hours the test was again interrupted to check the filter element. The element was found to be still servicable and only slightly clogged. The element was nevertheless cleaned and reinstalled.

Another shutdown occurred at 332 hours. This was occasioned by leakage through the PTFE seal gasket on the filter body. From this point to the final shutdown at 1011 hours, operation was entirely nominal except for gas venting.

Table 20. LOOP TEST SUMMARY, SECOND RC-2

Test & fluid	RC-2 (second)
Outcome	fail - incompatibility
Dates	18 Dec. 1972 to 31 Jan. 1973
Duration (at temp)	1011 hr
Termination reason	time expired
Pumping rate	56 ccpm
O-ring elastomer	EPR rubber (Parker E515-8)
Zero time exceptions*	
Forerun	285 hr @ 720°F, dist. H_2O
Condenser ferrules	-
Letdown valve	-
Filter	relocated to "X" Figure 6
Gas measurement	started at zero time
Vent glass tee	tubing tee replaced by 1/2" SS pipe tee
Fluid additions	38 cc
Vented gas	
Cumulative RTP volume	519 cc
Over span of	1011 hr
For average rate of	0.5 ccph
Filter changes	one (167 hr)

---

*exceptions to Table 16 or Appendix D

Gas evolution was experienced throughout the run. Cumulative volumes vented at RTP (room temperature and pressure) at various times were as follows:

Test hr	93	196	380	456	648	843	1011
cc Gas	112	156	270	290	374	459	519

When graphed, these data show an initial high gas evolution followed by a fairly steady rate of generation throughout the remainder of the test.

The test was rated a "fail" primarily because of the need to vent the hydrogen gas. While the water forerun failed to fully passivate the steel surface, it did greatly reduce the rate of reaction, as shown by the eight-fold reduction in the rate of gas evolution compared to the first RC-2 run.

Microscopic examination of internal heat exchange surfaces, exposed by slicing sections from each end of each coil, produced these observations:

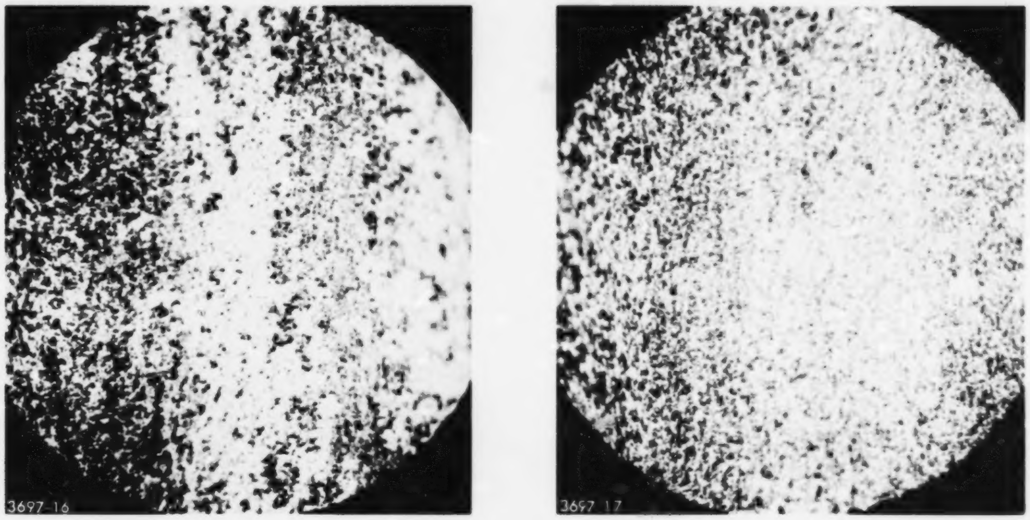
1. Heater inlet (cold) end (Figure 15a); smooth black oxide finish as in new tubing but with overlying tan-colored striations of a thin deposit extending downstream from a point 4 inches inside the heater shell; appearance suggests an inorganic material laid down when the fluid evaporates.

2. Heater outlet (hot) end (Figure 15b); smooth black oxide finish as in new tubing but covered with dense fine-grained coating of black crystalline material presumed to be magnetite, Fe_3O_4; this coating was much more dense (i.e. covered larger fraction of the visible surface), finer-grained and more tightly adherent to the substrate than that found in the same location after the first FC-2 test.

3. Condenser inlet (hot) end (Figure 15c); tan colored deposit filling in most of the original working marks (micro-scratches along tube axis) on the aluminum surface; color off-white when topping scraped off; deposit non-magnetic and tightly adherent.

4. Condenser outlet (cold) end (Figure 15d); same appearance as inlet section above.

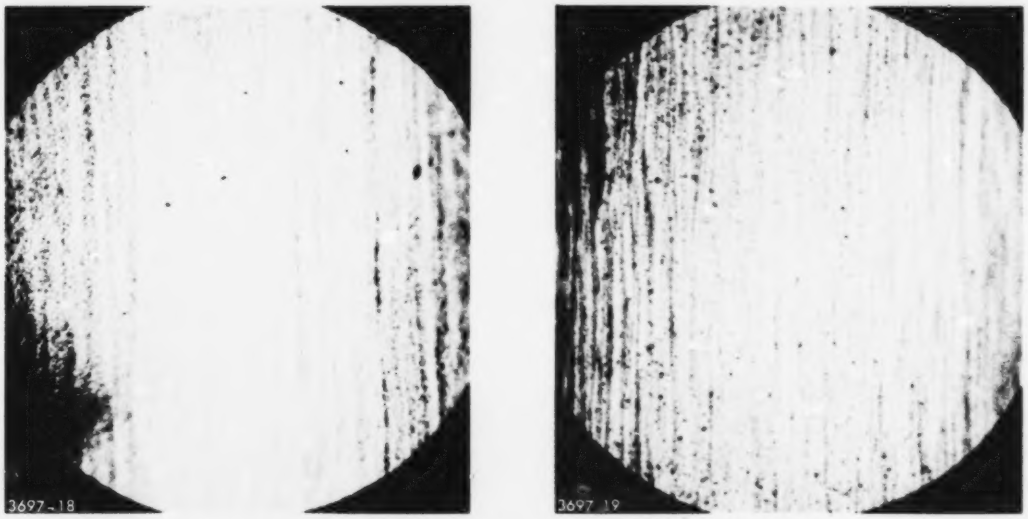
Fluid removed from the loop after 1001 hours of testing was deeply colored (deep amber) but relatively free of suspended solids.



15a. Inlet (Cold) End

15b. Outlet (Hot) End

Steel Heater Coil



15c. Inlet (Hot) End

15d. Outlet (Cold) End

Aluminum Condenser Coil

Figure 15. Photomicrographs of Heat Exchanger Surfaces after Second RC-2 Test (27x)

Comparisons of the gas-liquid chromatograms of new and used (1001 hours) fluid revealed only the subtlest of composition changes. The new fluid was found to have three minor peaks (contaminant species) in addition to the two major peaks (water and 2-methylpyridine). The used fluid showed the same three peaks but showed additionally a small amount of a higher boiling material. By area ratios the concentrations of the various tramp-compounds were as follows:

Species, Elution Time (min @ 100°C)	Concentration (ppm)	
	New Fluid	Used Fluid
3.1 ± .15	1800	1800
4.8 ± .2	1700	960
5.1 ± .25		
8.4 ± .3	0	370

By way of comparison, the water peak elutes at 1.4 minutes (with an exponential tail extending well past 14 minutes) and the 2-methylpyridine peak at 3.8 ± 0.2 minutes. (The chromatograph column consisted of a 4 meter length of 1/4-inch OD tubing packed with SE-52 on high performance Chromosorb W - helium carrier, thermal conductivity detector.)

The chemical identities of the minor contaminants were not determined.

5.5.2 Capsule Compatibility Tests at 300°F

In a real Rankine engine, as opposed to the dynamic loops of Section 5.5.1, a wider variety of materials must be in contact with the working fluid, and the question of compatibility of the working fluid with different materials arises. Welded low carbon and low alloy steels are the preferred materials in the hot, high pressure portion of the cycle. Many other materials, including elastomers, plastics, and bearing and sealing elements, are required in the cooler parts of the cycle to facilitate power transfer, carry moving loads, seal against leakage, and so on.

Capsule tests at 300°F were selected to test the compatibility of the final candidate working fluids with representative materials. Capsules constructed of stainless steel and having internal dimensions of 1.5 in. D x 5.5 in. long were used in this work. Into a capsule were placed the previously weighed solid specimens and then 30 cc of the liquid sample. The capsule was then closed off with a PTFE-sealed screw cap and placed in a 300°F thermostated oven for 164 hours. At the end of this time the capsules were removed, cooled, opened and inspected. Solid specimens were weighed again and the changes in weight and appearance noted. Results are summarized in Tables 21 and 22.

5.6 TOXICITY

The problem of assessing toxicological hazard is a complex one. It may be assumed that accidental and uncontrolled personal contacts with automotive working fluids would inevitably follow any widespread adoption of Rankine cycle automobiles. The hazard of such a contact, whether it occur via the skin, eyes, respiratory system or digestive tract, may be thought of as a product of an inherent toxicity times a dosage factor times the probability of reaching that dosage. As an example, the 50% lethal dose (LD_{50}) for table salt in rats is, by 1972 HEW data, 3 grams salt per kilogram body weight. A rat force-fed this amount of salt by stomach tube has a 50 percent probability of dying of acute salt poisoning. The probability of a rat accidentally ingesting this much salt is extremely small. Therefore, despite its inherent toxicity, table salt ranks far below cats in a listing of every day hazards faced by the rat population.

Considering how a working fluid might be manufactured, stored, transported, charged, used, serviced and replaced, it seems clear that vapor inhalation is the single mode of accidental contact most difficult to prevent and most likely to occur. This suggests that the primary concern in consideration of possible toxic hazards should be with acute intoxication by vapor inhalation. A model was adopted to assist in estimating accidental vapor inhalation hazards for candidates RC-1 and RC-2.

5.6.1 Vapor Hazard Model

While a full assessment of toxic hazards is a monumental experimental undertaking beyond present resources, it nevertheless is desirable to quantify, even if very roughly, the likelihood of inhaling significant quantities of working fluid vapors. As a step in this direction, a "worst case" accident is visualized as follows: a Rankine passenger car suffers a front end collision which dumps on the ground 0.25 cubic feet of working fluid and entraps the occupants for 20 minutes within a few feet of the spilled fluid. A mathematical model describing the evaporation and dispersion of the working fluid was set up employing these assumptions:

1. spherical symmetry and directional uniformity
2. evaporating fluid puddle represented as a sphere of constant radius R_o
3. partial pressure equal to vapor pressure p^* at surface of "puddle" sphere

Table 21. CAPSULE COMPATIBILITY TESTS - RC-1

164 Hours at 300°F
in Final Candidate RC-1

Specimen	Capsule	Specimen Wt. (g) Initial	Specimen Wt. (g) Change	Notes
Brass	A	1.3258	0.0001	
Bronze (brg. type)	A	1.2895	0.0187	Sl. absorption
Silver solder	A	0.1745	0.0000	
Aluminum 3003	A	0.2114	-0.0001	
Teflon (O-ring)	A	1.9200	0.1394	Mod. absorption
Viton A (O-ring)	B	1.5932	1.3	High absorption
Fiberite FM 4005	B	0.2817	-0.0027	
Viton coated Dacron	B	0.1673	-0.0250	Separated
Polyimide	B	0.4438	0.0005	
Polypropylene	B	0.1171	-	Dissolved
Graphite	B	1.2938	0.0941	Mod. absorption
Ryton PPS	C	0.3222	0.0044	
Delrin	C	0.5824	0.0256	Turned yellow
Dacron fabric	C	0.0482	0.0007	
Silica gel	C	0.7615	0.1250	Mod. absorption

Note: Of the materials listed, the Viton coated Dacron and the polypropylene are definitely incompatible with RC-1. Delrin is questionable. Viton A tends to strongly absorb the fluid and swell, yet it was successfully used to seal the letdown valve in the 1100+ hour dynamic loop test. All other materials are considered compatible.

Table 22. CAPSULE COMPATIBILITY TESTS

164 Hours at 300°F
in Final Candidate RC-2

Specimen	Capsule	Specimen Wt. (g) Initial	Specimen Wt. (g) Change	Notes
Brass	A	3.9247	-0.0098	Dk. coating, some attack
Bronze (brg. type)	A	4.2332	0.0615	Sl. absorption
Silver solder	A	0.2559	0.0002	
Aluminum 3003	A	0.5913	-0.0008	Some attack
Teflon (O-ring)	B	1.9163	0.0082	Sl. absorption
Viton A (O-ring)	B	1.6076	-	Disintegrated
Fiberite FM-4005	B	0.4645	0.0197	Mod. absorption
Viton coated Dacron	C	0.3829	-	Disintegrated
Polyimide	C	5.7022	-	Black coating
Polypropylene	C	0.6655	0.0420	Embrittled
Graphite	D	1.3514	0.0574	Mod. absorption
Ryton PPS	D	2.4566	0.1014	Mod. absorption
Delrin	E	3.6003	-	Dissolved
Dacron fabric	E	0.1896	-	Dissolved

Note: These data show that RC-2 is more difficult to confine. Viton, polypropylene, Delrin, Dacron and polyimide are incompatible under test conditions. Brass (and copper) should be considered unsuitable. Ethylene-propylene rubber is a suitable elastomer with RC-2, as proven in the 1000+ hour dynamic loop test.

4. No vapor in atmosphere at time zero
5. Fick's Law of diffusion applicable, with diffusivity D (interpreted as an eddy diffusivity in the absence of an average wind)

With these assumptions, the vapor concentration as a function of time and distance is given by the diffusion equation as:

$$p = \frac{R_o p^*}{r} \operatorname{erfc}\left(\frac{r-R_o}{2\sqrt{Dt}}\right) \qquad (1)$$

where p = partial pressure of working fluid in air

p* = vapor pressure of working fluid

R_o = radius of the spilled sphere

r = distance from center of spill

D = diffusivity

t = time

erf = error function

erfc = 1-error function (proportional to the integral of the normal probability distribution)

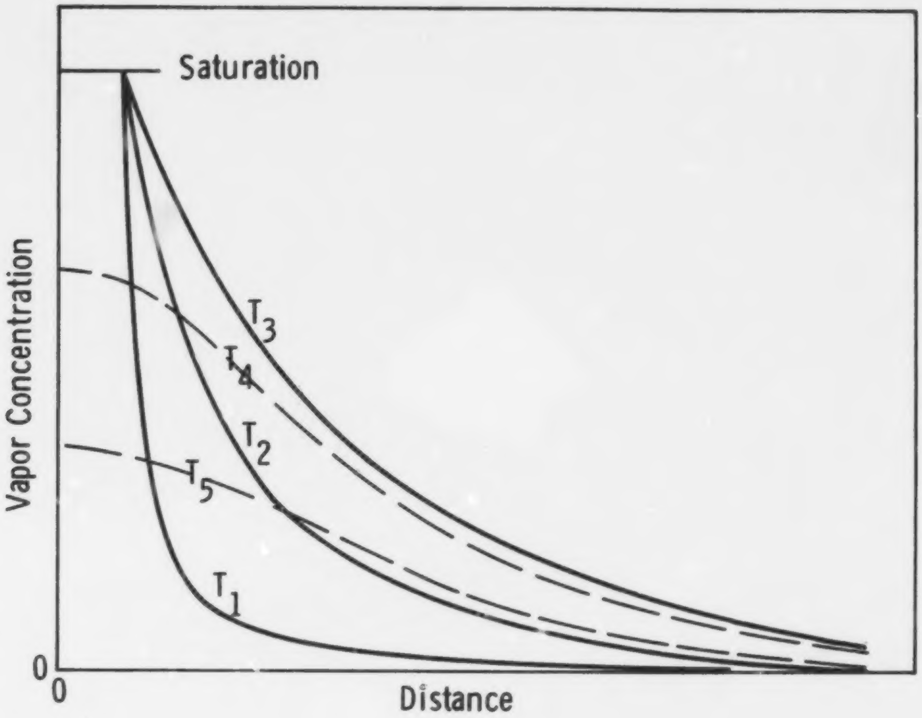
This is illustrated in Figure 16 where it is seen that at various times (T_1, T_2, T_3, etc.) the concentration of vapor with distance from the spill would vary in the manner shown. Eventually the puddle would dry up and the concentration profiles then would decay in the manner of curves T_4 and T_5.

At infinite time, the asymptotic (maximum) concentration in air is given by

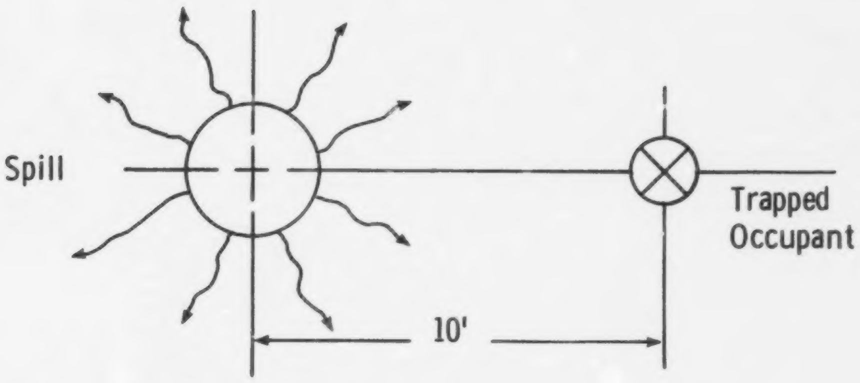
$$p_\infty = \frac{R_o}{r} p^* \qquad (2)$$

However, the spill could not last an infinite time, nor would trapped occupants remain at the scene an infinite time. Although there is no analytic solution for the exact lifetime of the puddle, the rate of evaporative disappearance of spilled liquid, in terms of the change of radius of a shrinking liquid source sphere, is given by

$$\frac{dR}{dt} = -\frac{MDp^*}{\rho R_G T}\left[\frac{1}{\sqrt{\pi Dt}} + \frac{1}{R}\right] \qquad (3)$$



Concentration Profiles



Plan View

Figure 16. Vapor Inhalation Hazard Model

where M = molecular weight of working fluid,
ρ = its density,
R_G = the ideal gas law constant, and
R = instantaneous puddle radius.

A conservative estimate of the puddle life is obtained by assuming R in the $1/R$ term to be constant at R_o. The puddle life then is somewhat less than

$$t_D = \frac{R_o^2}{\pi D}\left(1 + \sqrt{1 + \frac{\pi \rho RT}{Mp^*}}\right)^2 \qquad (4)$$

After time t_D, the source of vapor no longer exists. An approximation of p vs t at $t = t_D$, assuming no further vapor generation, yields the subsequent vapor dispersion by the formula

$$p = \frac{R_o p^*}{r} \operatorname{erfc}\left(\frac{r-R_o}{2\sqrt{Dt_D}}\right) \operatorname{erf}\left(\frac{r-R_o}{2\sqrt{D(t-t_D)}}\right) \qquad (5)$$

Thus, equation (1) applies when $t < t_D$, equation (4) estimates t_D, and equation (5) applies when $t > t_D$. The maximum concentration at any time-position point is given by equation (1) at $t = t_D$.

In the calculations reported here, it was assumed that the "occupants" were trapped for 20 minutes at an effective distance from the spill of ten feet (actual distance six feet plus four feet allowed for shielding effect of enclosure). The amount of fluid spilled was assumed to be 1.9 gallons (0.25 cubic feet) and the diffusivity was varied over a wide range of values.

Effective atmospheric diffusivity varies considerably, depending on conditions. However, in a region near the ground and near a spill, a value of 18 cm^2/sec appears to be a reasonable choice for the hypothetical worst case accident. This was derived from data given by Turner (ref. 5). Calculations presented here cover a substantial range above and below this value. The principal results are presented in Tables 23 to 25. The first two of these show average concentration and "dose" (or concentration integrated over the 20-minute time interval) for each of the candidate fluids as influenced by diffusivity. It is interesting to note that there is a maximum "dose" in each case at some high value of diffusivity. Table 25 shows the concentration as a time function at a single diffusivity for both candidates.

Table 23. VAPOR DISPERSION CALCULATION

Fluid: Final Candidate RC-1 (fluorobenzene mixture)

Molecular Weight	175.3
Molecular Diffusivity*	0.0585 cm^2/sec
Ambient Temperature	70°F
Vapor Pressure	0.169 atm. abs.** (169,000 ppm)
Fluid Density	1.58 g/cm^3

Assumed Diffusiv., cm^2/sec at 10 ft distance:	1.	4.	16.	64.	256.	1024.
20 min. "dose," ppm-min.	0.2×10^{-4}	59.8	6300	34,700	54,900	28,200
Average conc., ppm	0.9×10^{-6}	3.0	315	1,730	2,740	1,410

* Method of Fuller, Schettler and Giddings, (ref. 6) assuming $(\Sigma v)_M = x_1(\Sigma v)_1 + x_2(\Sigma v)_2$

** Taken at a temperature midway between normal boiling point and 70°F

Table 24. VAPOR DISPERSION CALCULATION

Fluid: Final Candidate RC-2 (2-methylpyridine/water)

Molecular Weight	44.3
Molecular Diffusivity*	0.144 cm^2/sec
Ambient Temperature	70°F
Vapor Pressure**	0.110 atm. abs. (equiv. conc. 110,000 ppm)
Fluid Density	0.950 g/cm^3

Assumed Diffusiv., cm^2/sec at 10 ft distance:	1.	4.	16.	64.	256.	512.
20 min. "dose," ppm-min.	0.00	38.9	4100	22,600	46,100	56,000
Average conc., ppm	0.00	1.95	205	1,130	2,310	2,800

* Method of Fuller, et al. (see footnote, Table 23).

** Taken at a temperature midway between normal boiling point and 70°F.

Table 25. VAPOR DISPERSION CONCENTRATION HISTORIES

Assumed Diffusivity 18 cm^2/sec
Distance from Spill 10 feet
See Tables 23 and 24 for other properties

Time Since Spill, min.	Concentrations, ppm RC-1	Concentrations, ppm RC-2
0	0.00	0.00
2	0.055	0.036
4	10.8	7.0
6	66.6	43.4
8	171	111
10	306	199
12	455	296
14	609	396
16	761	495
18	908	591
20	1049	683
20 min. avg. conc.	390 ppm	254 ppm

5.6.2 Rat Inhalation Studies

As already noted, inhalation of working fluid vapors represents the most likely avenue of accidental exposure. A search of the literature revealed a paucity of information regarding vapor toxicity of the methylpyridines. In the case of RC-1 some data, mainly concerned with the anesthetic and analgesic action of highly fluorinated benzenes, were available (ref. 7 to 11). These investigations indicated that vapor toxicity of penta- and hexafluorobenzenes is quite low. A Russian investigator (ref. 12) reported the median 2-hr lethal air concentration (LC_{50}) of hexafluorobenzene with white mice is 95 mg/liter (12,500 ppm) as compared to 37 mg/l (13,700 ppm) for benzene itself.

In the present investigation, 4-hr LC_{50} rat inhalation determinations were made with both final candidate fluids. Complete details of these experiments are given in Appendixes E and F. Table 26 summarizes pertinent features of the experiments and the LC_{50} results. Here a comparison is also made between the exposure levels calculated from the vapor dispersion model for a 20-minute exposure at 10 ft from a spill (Table 25) and the 4-hr rat LC_{50}'s. Under conditions set forth for the model, a substantial margin of safety is indicated.

Table 26. RAT INHALATION STUDIES: 4-HOUR LC_{50} CONCENTRATIONS

Experimental Conditions:

10 Rats per Test

70 Liter Chamber

Air Flow Changes Air Every 3-6 Minutes

Test Fluid Metered into Vaporizer and Thence Carried into Chamber by Air Stream

4-Hour Exposure Time per Test

Concentrations Increased in Subsequent Tests Until Sufficient Data to Calculate LC_{50}

After Exposure Surviving Rats were Observed for 14 days

4-Hour LC_{50} Results

RC-1 (Fluorobenzenes) LC_{50} = 115 mg/l or 16,000 ppm

RC-2 (2-MP-H_2O) LC_{50} = 14.3 mg/l or 8,000 ppm

Comparison With Calculated Exposure Levels:

	RC-1	RC-2
Average 20 min. Dosage @ 10 ft	390 ppm	254 ppm
4-Hour LC_{50} (For Rats)	16,000	8,000

Subsequent to these results, additional mice inhalation work sponsored by Imperial Smelting Corporation has been reported (ref. 13). The full report is included in Appendix G. The principal results of 30-minute exposure tests were as follows:

Fluid	30-Minute LC_{50}, ppm (vol)
Pentafluorobenzene	30,000
Hexafluorobenzene	65,000
50:50 mixture of above	50,000

Considering that the exposures were 30 minutes rather than 4 hours, these data fall in line with the 4-hour RC-1 data.

Some appreciation for the inhalation hazards of these materials can be had by comparing their animal LC_{50}'s with concentrations of more familiar materials which have resulted in human death. Gasoline is reported (ref. 14) to have killed a man after 5 minutes exposure in a concentration estimated between 5000 and 16,000 ppm. Benzene is reported (ref. 15) to be lethal in 5 to 10 minutes at 19,000 to 20,000 ppm, and hazardous to life in 30 to 60 minutes at 7500 ppm. Both gasoline and benzene are handled in very large quantities every day with only the rarest reports of vapor intoxication.

Odor is an intangible but important factor in consideration of toxic hazards. Both final candidates have characteristic odors. RC-2 with its content of 2-methylpyridine is immediately detectable at very low concentrations by its strong, penetrating, and extremely disagreeable odor. Its escape into the atmosphere can be expected to strongly motivate people to move away from the source. RC-1 has a much milder, sweeter, medicinal odor which would likely produce a positive but less urgent motivation to move.

5.6.3 Range Finding Toxicity Tests

Considerably more information about oral toxicity of pyridine and methylpyridines was available in the literature than could be found relating to the effects of vapor inhalation. Pertinent data and literature sources are summarized in some detail in Appendix H. Here it is sufficient to note that Veselov (ref. 16) reports the following acute oral toxicity levels for 2-methylpyridine:

LD_{50} = 674 mg/kg in mice
790 mg/kg in rats
900 mg/kg in guinea pigs

Closely bracketing these results are the toxicity parameters for rats given by Polilei (ref. 17) as:

$$LD_0 = 550 \text{ mg/kg}$$
$$LD_{50} = 790 \text{ mg/kg}$$
$$LD_{100} = 950 \text{ mg/kg}$$

Using white mice, Lapik and Zimina (ref. 18) report the oral LD_{50} of pentafluorobenzene as 710 mg/kg and that of pentafluoropyridine as 280 mg/kg. While pentafluorobenzene had a narcotic effect with decreased motor activity, pentafluoropyridine caused convulsions in the test animals.

Animal acute toxicity tests carried out in the course of this investigation included rat feeding and rabbit skin and eye contact experiments, as well as the rat vapor inhalation experiments covered above. Several fluids of interest other than the final candidates RC-1 and RC-2 were included in this test series.

In determining rat oral LD_{50} values, the test material was fed by stomach tube to mixed sex albino rats. The acute rabbit skin absorption test involved applying the test material in increasing doses to the closely clipped skin of white rabbits. The less severe rabbit skin irritation test was carried out by adding a single dose of test fluid to a one square inch area of skin and awarding an irritation score after a 24-hr exposure period. Eye irritation in rabbits was determine by adding 0.1 milliliter of sample to the conjunctival sac of the right eye of the test animals; from this an eye irritation score was determined over a 7-day exposure period. Results of these tests are summarized in Table 27. Complete data are given in Appendix I.

Table 27. ACUTE TOXICITY TEST RESULTS

		LD_{50} (mg/kg)		Irritation Score	
Fluid	Mol %	Rat Oral	Rabbit Dermal	Rabbit Skin①	Rabbit Eye②
2-Methylpyridine/H_2O (RC-2)	40/60	810	200-316	5.6	71
3-Methylpyridine/H_2O	40/60	710	126-200	5	67
4-Methylpyridine/H_2O	40/60	700	200-316	4.6	77
4-Methylpyridine (undiluted)	100	700	126-200	Corrosive	72
$C_6F_6/C_6HF_5$③ (RC-1)	40/60	~12,000	>8000	3	10
C_6F_6/C_6F_5N④	40/60	310	~5000	5.3	62

Notes: ① Maximum score = 8
② Maximum score = 110
③ Hexafluorobenzene/pentafluorobenzene
④ Hexafluorobenzene/pentafluoropyridine

5.6.4 Products of Combustion

A question often raised in considering working fluid toxicity is whether exposure of the fluid to fire is likely to generate toxic materials which then pose a greater threat to safety than the fire itself. The appearance of phosgene in the products of oxidative pyrolysis of certain chlorine-bearing organic fluids is an oft-cited example.

As in the case of the unburned working fluid, the most likely route of acute intoxication by combustion products is by inhalation. Most of the comments of Section 5.6.1 on vapor dispersion apply equally to these materials when allowance is made for the fact that they are formed in the gaseous state. To establish that a real hazard can exist, it is not sufficient to show that hazardous substances are formed. It must also be shown that dangerous concentrations of these substances can reasonably be expected to be generated and persist for sufficient time to cause injury to an incapacitated victim.

In interpreting the combustion experiments to follow, it must be kept in mind that the products of combustion of the working fluids were confined within a small chamber to simplify identification and measurement. Concentrations reported are, therefore, far in excess of those to be expected in an actual incident. Hazards are to be assessed only after realistic air dilutions are established.

5.6.4.1 Experimental Procedure - The final candidate fluids were burned in an Aminco-NBS smoke density chamber (ref. 19) of 18 cu ft volume. A measured amount of the liquid was transferred from a syringe into a stainless steel sample holder of special design. The sample was moved into position so that the surface of the liquid was directly impinged upon by the flames from a six-outlet propane/air burner. The flow rates of propane and air were 94 cc/min and 647 cc/min, respectively.

The combustion gases were confined in the chamber whose internal wall temperature was maintained at approximately 50°C. At the completion of burning, the burners were extinguished, and measured volumes of the contained gases were withdrawn into evacuated vessels through a sampling port in the ceiling of the cabinet.

A minimum of two experiments were conducted with each candidate fluid. From one to two liters of gas were withdrawn for each analysis.

The temperature of the flames produced during combustion of the fluids were measured with an optical pyrometer.

5.6.4.2 Analytical Methods - Carbon monoxide and total hydrocarbon concentrations were measured with the Monsanto $CO/CH_4/C_xH_y$ Analyzer, which is a gas chromatographic type instrument

Hydrogen cyanide, which could be generated during the burning of the water/2-methylpyridine mixture, was sampled by withdrawing a known volume of the combustion gases through a tube packed with Ascarite absorbent (asbestos impregnated with NaOH). The Ascarite was dissolved in water. An accurate and sensitive fluorometric method, adapted from procedure outlined by Hanker, J. S., et al. (ref. 20), was used for cyanide analysis. Parallel fluorometric measurements were conducted with standard cyanide solutions.

Hydrogen fluoride, produced by the burning of the penta- and hexafluorobenzene mixture, was sampled by withdrawing measured volumes of the combustion gases through a Teflon tube, packed with Ascarite. The fluoride was quantitatively extracted and measured as fluoride ion, using a specific fluoride ion electrode.

Nitrogen oxides (NO_x), from the burning of the water/2-methylpyridine mixture, were collected by withdrawing a measured volume of the combustion gases into an evacuated vessel containing a dilute sulfuric acid/hydrogen peroxide absorbing and oxidizing solution. The nitrogen oxides ($NO + NO_2$), except nitrous oxide (N_2O), were measured colorimetrically using the phenyldisulfonic acid (PDS) procedure (ref. 21).

The mass spectra of the combustion gases, other than water, carbon dioxide, and the gaseous products referred to above, were recorded with a Consolidated Engineering Co. Model 21-103C mass spectrometer.

5.6.4.3. Results and Discussion - Experimental and analytical results are given in Tables 28 through 30. Referring to Table 28, it is seen that combustion gases from the burning of RC-1 with propane-air are relatively high in CO and HF, both recognized toxic substances. It appears that the presence of the working fluid significantly inhibited the complete combustion of the propane, as evidenced by the high CO and unburned hydrocarbon (C_xH_y) concentrations.

Combustion of RC-2 was, as might be expected, more complete. Much lower concentrations of the toxic materials CO, NO_x and HCN were found. Also, the measured flame temperature was somewhat higher.

Mass spectrometric analyses of additional products of combustion of the two fluids, shown in Tables 29 and 30, fail to reveal any comparably hazardous concentrations.

Table 28. COMBUSTION EMISSION EXPERIMENTS

Fluid	Average Sample Mass (g)	Burning Time (min)	Flame Temp. During Burning (°C)	CO (ppm)	C_xH_y (ppm)	HF (ppm)	NO_x (ppm)	HCN (ppm)
RC-1	3.51±0.30	1.5-2.0	1100-1145	612±66	935±72	746±80	-	-
RC-2	2.45±0.26	3.0	1185-1250	30±1	49±17	-	79±6	<0.5

Table 29. MASS SPECTROMETRIC ANALYSIS OF RC-1 COMBUSTION PRODUCTS*

Component	Concentration (ppm by vol.)
Hexafluorobenzene	57
Pentafluorobenzene	68
Tetrafluorobenzene	46
Silicon tetrafluoride	18
Perfluoromethane	42
Perfluoroethane	18
Carbonyl fluoride	1.1

*This table does not include data for H_2O, CO_2, CO, NO_x, and HF content of the chamber atmosphere.

Table 30. MASS SPECTROMETRIC ANALYSIS OF RC-2 COMBUSTION PRODUCTS*

Component	Concentration (ppm by vol.)
Methane	2.4
Ethylene	3
Ethane	12
Propane	20
Propylene	5

*This table does not include data for H_2O, CO_2, CO and NO_x content of the chamber atmosphere.

5.7 FLAMMABILITY

Flash and fire points, and autogenous ignition temperatures measured using the final candidates and related compositions are listed in Table 31. Comparable literature values for a number of familiar reference fluids are also listed for comparison. The data show RC-1 to be non-flammable, and RC-2 to be flammable, in terms of these specific tests. RC-2 has flash and fire points comparable to kerosene despite a higher vapor pressure. The effect of the water content of this fluid is to raise its flash and fire points about 45°F above straight 2-methylpyridine.

Flammabilities of the ingredients of RC-2 are presented by Pollard (ref. 22). He shows that all fluorobenzenes containing four or more fluorine atoms per molecule are non-flammable in air under any conditions.

Results of a hot compartment ignition test are listed in Table 32 for the final candidates in comparison with benzene and Fluorinol 85 (a product of Halocarbons Incorporated). In this test, a pressurized spray of the fluid is admitted into a heated, air-filled chamber equipped with a continuous high-voltage spark gap. The intensity of ignition is gaged by the reading of the shock meter, which is simply an accelerometer attached to a loose sheet metal lid covering the compartment. A bare thermocouple within the chamber gives an indication of the amount of heat generated upon ignition.

The results show RC-1 to be practically inert compared to RC-2 and Fluorinol 85 (which are quite comparable in both energy release and shock intensity) and far below benzene. RC-2 shows temperature rises somewhat greater than benzene but shock intensities about half as high. The shock meter readings are measures of the sharpness of combustion and are indicative of damage potential.

Test methods are covered in detail in Section 6.7.

5.8 LUBRICATION AND LUBRICANTS

Lubricant requirements of a Rankine cycle power plant employing a reciprocating expander are substantially different and much more stringent than the demands of a turbine expander system. In the latter the main bearings can be mechanically isolated from contact with the working fluid and they operate at relatively low temperatures. Thus conventional lubricants can be used. Demands of the reciprocating expander are another matter. Here it is almost impossible to mechanically isolate the lubricant from the

Table 31. FLASH AND FIRE POINTS AND AIT'S OF FINAL CANDIDATES RC-1 & RC-2 AND REFERENCE FLUIDS

Fluid	Flash Point (°F)	Fire Point (°F)	AIT (ASTM D-2155) (°F)
Final Candidate RC-1	None	None	None*
Final Candidate RC-2	130	145	1060
Additional mixtures of water and 2-methylpyridine			
Mol % 2-methylpyridine			
100	90	100	
75	90	105	
40	120	145	
15	135	175	
Reference Fluids			
Gasoline	-50		
Benzene	12		928
Toluene	40		900
Kerosene		100-160	
Ethyl alcohol	55		685
Methyl alcohol	55		727
Ethylene glycol	232		748

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*Up to 1200°C., the apparatus limit

Table 32. HOT COMPARTMENT IGNITION TEST RESULTS

Test conditions:	
Fluid charge	30 cc
Compartment temp.	100°C
Compartment environment	Air
Spray time	1/4 sec

	Fire Results					
	1000 psi Spray		500 psi Spray		100 psi Spray	
Working Fluid	Δ Temp (°C)	Shock Meter	Δ Temp (°C)	Shock Meter	Δ Temp (°C)	Shock Meter
Benzene	58	14	80	11	138	3
RC-1	-19	0	-13	1	9	1
RC-2	72	8	103	4	159	2
Fluorinol 85	73	9*	84	6*	80*	0*

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*Delayed Ignition or Fire

working fluid. As a consequence, some minor amount of lubricant is inevitably carried through the vaporizer. To avoid fouling the vaporizer and degrading the lubricant, it is necessary that the latter have thermal stability comparable to the working fluid. Vaporizer temperatures in the 710-720°F range required in the present study exceed the thermal stability of conventional mineral oil lubricants. This means that a highly stable synthetic lubricant must be employed. Since 2-methylpyridine/water of 0.35 mol fraction 2-methylpyridine, or similar mixtures with the other methylpyridines, appear to be optimum for a reciprocating Rankine system, the lubricant must further be both thermally and chemically stable in such a water-amine environment up to ∿720°F. Finally, it is desirable that the lubricant and working fluid have low mutual solubility; that is, the oil should be insoluble in the working fluid and vise versa so as to minimize both dilution of the crankcase oil by working fluid and carryover of lubricant to the vaporizer. Given these restrictions, lubricant choices are extremely limited.

Although mutual insolubility of the working fluid and lubricant is desirable, system design can reduce working fluid contamination by tight seal design in the pump and expander with lubricant separation before working fluid condensation. Since the bulk lubricant operational temperature can be higher than the working fluid boiling point under anticipated crankcase pressures, the working fluid would not dilute the lubricant significantly during vehicle operation. Only on shutdown does lubricant dilution seem possible and this could be corrected by appropriate one-way valving between the lubrication system and the Rankine cycle system.

5.8.1 Lubricant Stability

A test program was initiated, a) to measure relative solubilities of methylpyridine-water working fluids in various potential lubricants, and b) to determine thermal stability (compatibility) of various combinations. The ampoule test described in Section 6.3 was used for the thermochemical stability work, and a simple procedure was devised to measure relative solubility of the methylpyridine-water fluids in the lubricant.

> Procedure: Four grams of the test lubricant in a 25 x 100 mm test tube were stirred vigorously for 10 min. with 12 g of the methylpyridine-water working fluid. The mixture was then allowed to stand undisturbed for 10-15 min. to allow lubricant and working fluid layers to separate. After settling, about 1 g of the working fluid layer was withdrawn and carefully weighed. The weighed sample was then dissolved in about 10 cc of glacial acetic acid and titrated with 0.1 N perchloric acid (in acetic acid solution) using

crystal violet indicator. The amount of amine dissolved in the lubricant layer could then be calculated from the amount of perchloric acid consumed.

Results of lubricant-working fluid solubility studies are summarized in Table 33. Here it can be seen that only the perfluorinated oils (experiments 5, 6 and 7) have the requisite insolubility properties, with hydrocarbon mineral oils (11-15) being next in solubility. Unfortunately both these oils are unstable at 720°F as are all of the other candidates tested except for the simple aromatic hydrocarbons. This is essentially what might be predicted on the basis of known thermal stability behavior (see section 6.2.1). Only the biphenyl-terphenyl eutectic (whose composition is roughly 21% biphenyl, 47% o-terphenyl, and 32% m-terphenyl) seemed sufficiently available for lubrication studies.

5.8.2 Lubrication Wear Tests

After the lubricant stability tests indicated that the only 720°F stable fluid was the biphenyl-terphenyl eutectic, and considering the lubricant volumes need for testing, the lubrication tests were performed in two stages:

1. Screen six composite materials as sealing ring materials for wear resistance at 600°F on cast iron in the biphenyl-terphenyl eutectic.

2. Select the best composite material and run with an alloy steel, M50, on cast iron at 600°F; and at room temperature with mixtures of the biphenyl-terphenyl eutectic and RC-1 and RC-2.

The apparatus used in these test was a Monsanto Company developed wear test referred to as the Rub Block Test and as described in detail in Appendix J. Essentially, the apparatus consists of two flat blocks (ring material) loaded diametrally against a rotating ring (cylinder block material). This assembly is immersed in the test lubricant which in turn, is contained in a hermetically sealed chamber provided with fluid temperature and pressure controls. Examination of the wear scars developed on the rubbing blocks quantitatively ranks the lubricants and wearing materials. The texture of the scar can distinguish the types of wear taking place.

The results from composite material testing are presented in Table 34 with photographs of the ring and blocks in Figures 17 through 19. A correlation between scar width and carbon porosity is demonstrated in Figure 20.

Table 33. EQUILIBRIUM SOLUBILITY OF METHYLPYRIDINE WORKING FLUIDS IN VARIOUS PROSPECTIVE LUBRICANTS

Potential Lubricant	Mole Fraction Amine in Working Fluid Used for Equilibration	Wt Percent Amine in Lubricant Phase after Equilibration at 77°F (25°C)	Results of Thermal Stability Tests at 720°F
1) biphenyl-terphenyl eutectic	0.3 2-methylpyridine 0.4 2-methylpyridine	24.2 32.9	Stable 168 hr @ 720°F, but only single phase on cooling
2) OS-124 5-ring polyphenyl ether	0.3 2-methylpyridine 0.3 2-methylpyridine	17.6 24.1	Extensive decomposition 168 hr @ 720°F
3) F-2557, 4-ring mixed S- and o-polyphenyl ether	0.3 2-methylpyridine 0.4 2-methylpyridine	18.0 25.2	Extensive decomposition 168 hr @ 720°F
4) tetramethyldi(m-phenoxyphenyl)disiloxane [m-ØOØSi(CH$_3$)$_2$]$_2$O	0.3 2-methylpyridine 0.4 2-methylpyridine	17.4 23.5	Extensive decomposition 168 hr @ 720°F
5) perfluorokerosene	0.4 2-methylpyridine	0.24	Complete decomposition 168 hr @ 720°F
6) Krytox AB perfluoro ether	0.4 2-methylpyridine	0.1	
7) Krytox AD perfluoro ether	0.4 2-methylpyridine	0.02	
8) o/m-terphenyl-phenoxybiphenyl 1/2 mixture	0.4 2-methylpyridine	32.9 -	Partial decomposition 168 hr @ 720°F
9) 1-phenylnaphthalene	0.4 2-methylpyridine	36.1 -	Not tested - should be stable
10) o/m-terphenyl + bisphenoxybiphenyl	0.4 2-methylpyridine 0.4 3-methylpyridine 0.4 4-methylpyridine	29.5 32.1 26.7	Partial decomposition 168 hr @ 720°F
11) SUNISO 3GS hydrocarbon oil	0.4 3-methylpyridine	8.6	Partial decomposition 90 hr @ 720°F
12) TECO Oil #1, hydrocarbon	0.4 3-methylpyridine	7.1	
13) TECO Oil #2, hydrocarbon	0.4 3-methylpyridine	7.1	
14) TECO Oil #3, hydrocarbon	0.4 3-methylpyridine	7.2	
15) TECO Oil #4, hydrocarbon	0.4 3-methylpyridine	5.6	
16) DC 710 Silicone oil	0.4 3-methylpyridine	14.7 -	Complete decomposition 90 hr @ 720°F

Table 34. RUB BLOCK WEAR TESTS OF COMPOSITE MATERIALS

Test Conditions:

Ring diameter = 1.5 in.
Block thickness = 0.25 in.
Ring speed = 3200 rpm
Load between blocks and ring = 44.2 lb_f
Test duration = 50 min.
Lubricant = Biphenyl-terphenyl eutectic
Fluid temp. = 600°F.
Ring material = cast iron*

Test No.	Block Material	Scar Width (in.)
1	Pure carbon P-19	0.112
2	Pure carbon P-5-NR	0.183
3	U. S. Graphite 14SC	0.094
4	U. S. Graphite 110	0.098
5	Ford I/G (40/60), 16% porosity	0.477
6	Ford I/G (40/60), 12% porosity	0.387

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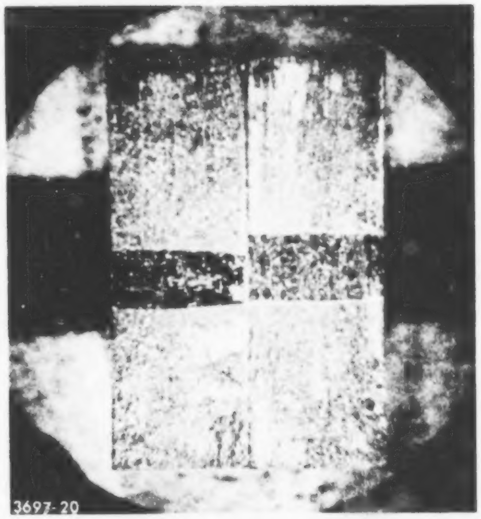
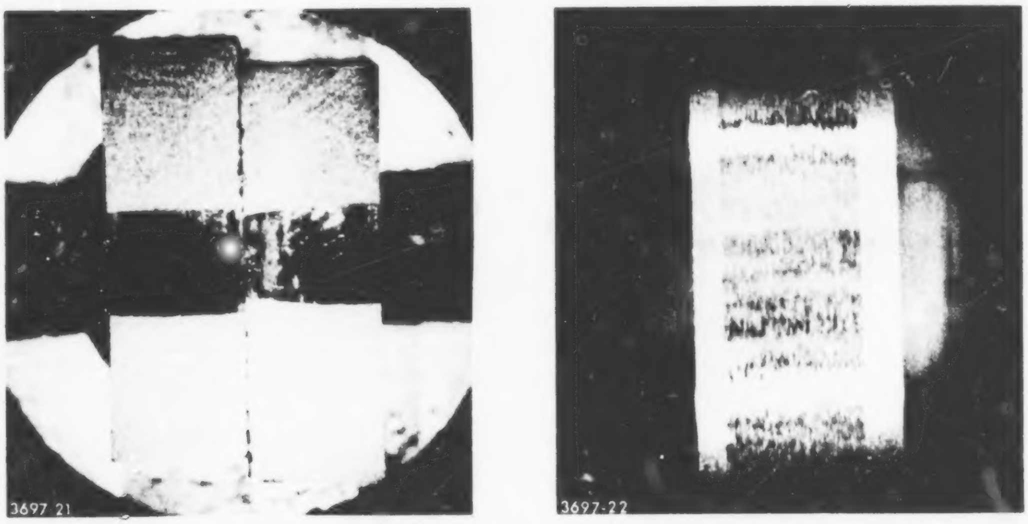
*Ford Cast Iron Material ESE-MIA117-B
Hardness Rc 50, case depth = 0.025 in.
Surface finish direction of rotation = 8-12μ in RMS



17a. P-19 Blocks

Test 1

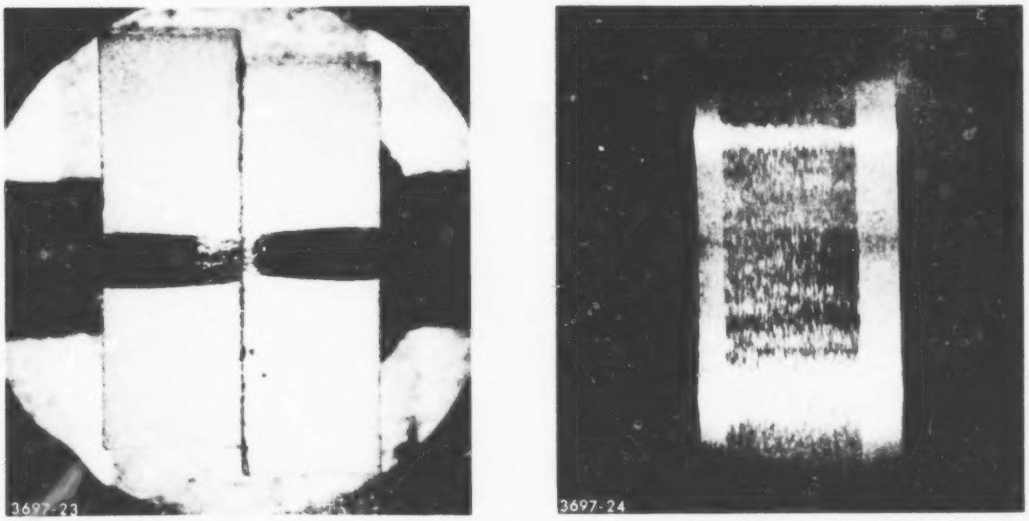


17b. P-5-NB Blocks

17c. Cast Iron Ring

Test 2

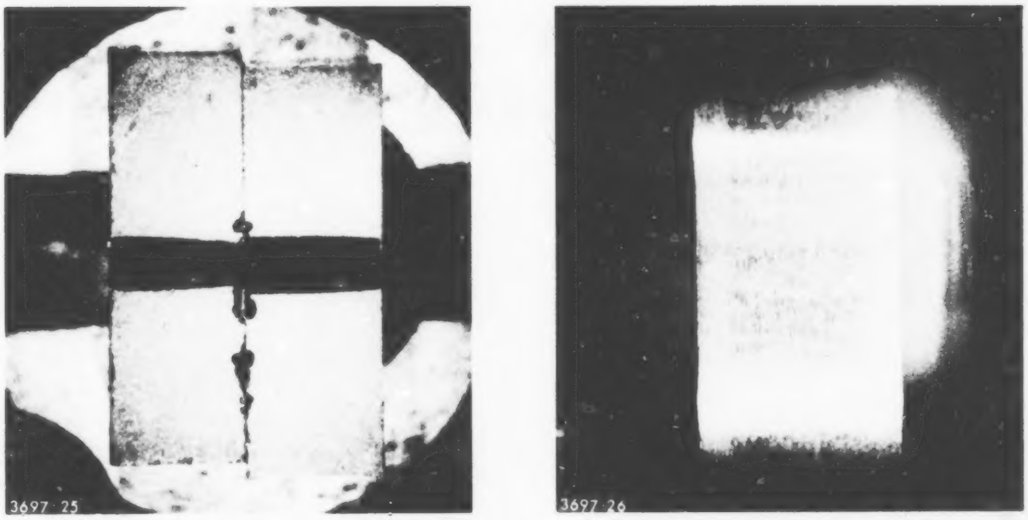
Figure 17. Rub Block Wear Specimens (3.2x)



18a. 14SC Blocks

18b. Cast Iron Ring

Test 3

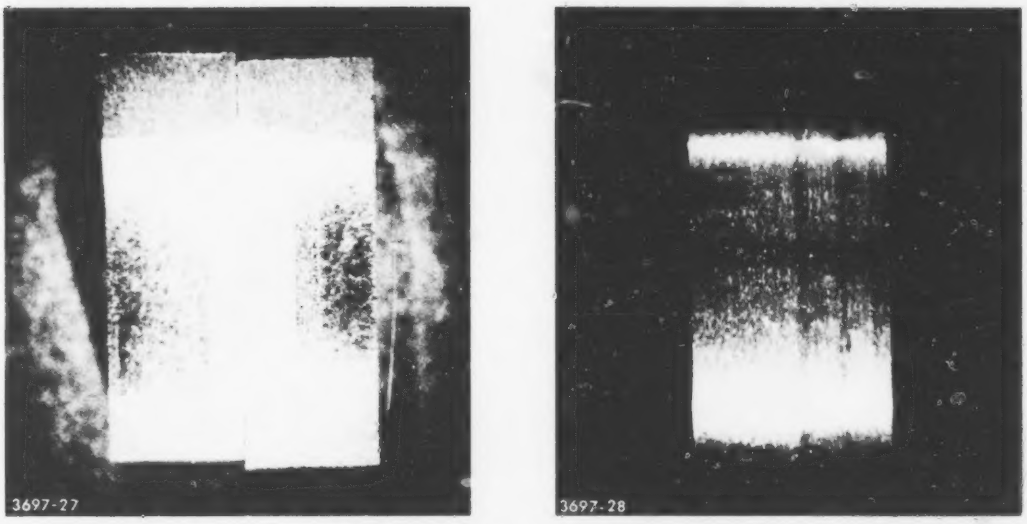


18c. 110 Blocks

18d. Cast Iron Ring

Test 4

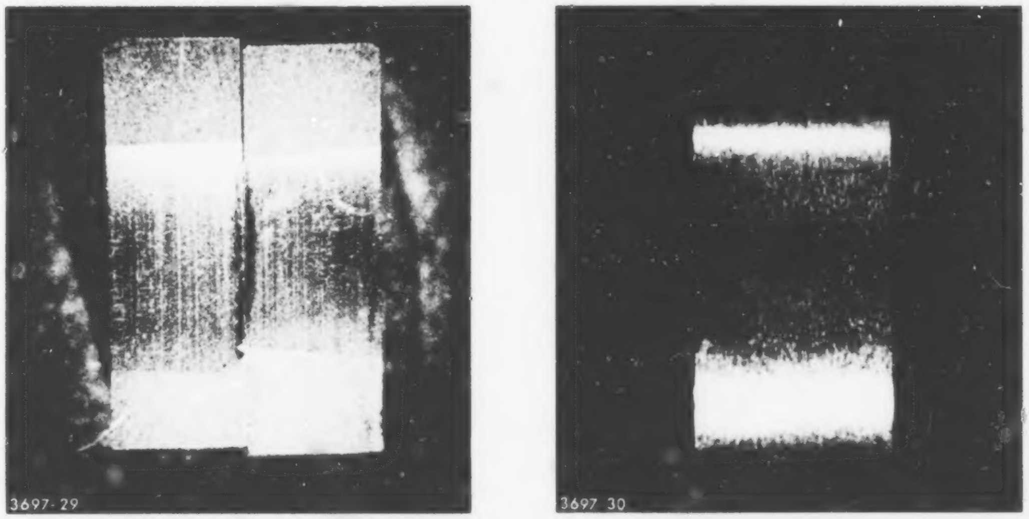
Figure 18. Rub Block Wear Specimens (3.2x)



19a. I/G (40/60) 16% Porosity Blocks

19b. Cast Iron Ring

Test 5



19c. I/G (40/60) 12% Porosity Blocks

19d. Cast Iron Ring

Test 6

Figure 19. Rub Block Wear Specimens (3.2x)

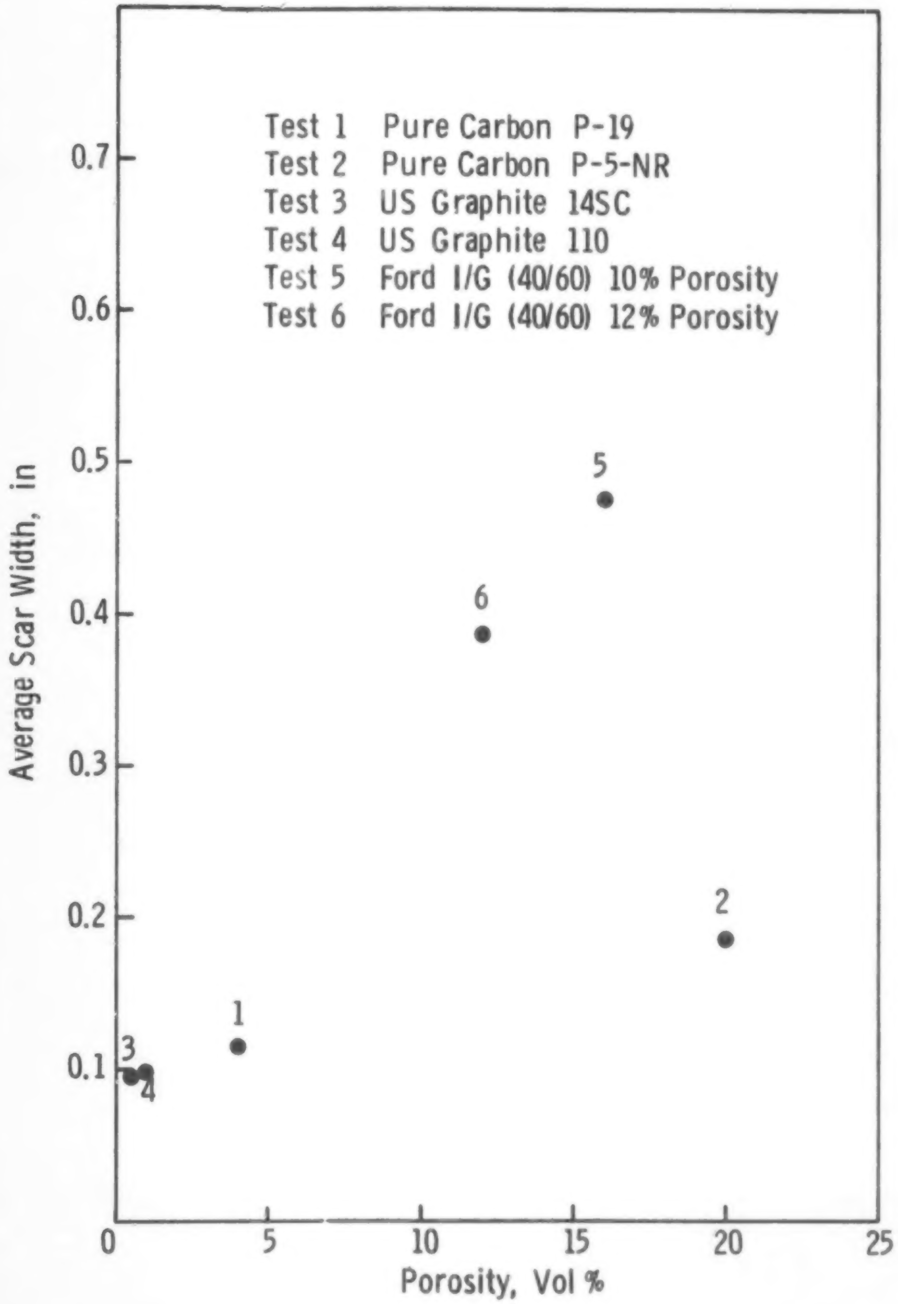


Figure 20. Scar Widths of Carbon Blocks versus Porosity

The U.S. Graphite 14SC sintered graphite material was chosen as the best composite to run with the lubricant working fluid mixtures. The others evaluated had larger scar widths but should not be considered inferior to USG 14SC since the 44.2 lb_f normal load is extremely high for non-conforming contacts. Real piston rings would operate at much lower contact stress levels, but to expedite a short term wear test the higher load was needed. Also worthy of note is the low ring wear on the highly worn Ford I/G composites. This could translate to low cylinder wear in a Rankine reciprocating expander.

Since the biphenyl-terphenyl eutectic has a relatively high pour point of 50°F, it was hoped that a beneficial dilution with RC-2 would produce a lower flow point. Equal parts of the lubricant and working fluid were found to have a flow point of -22°F (-30°C), and the mixture is in two phases at room temperature.

For mixtures of RC-1 and the biphenyl-terphenyl eutectic, a 5% dilution of the eutectic lubricant was chosen due to the limited availability of RC-1. The test conditions and wear results are presented in Table 35. Corresponding block and ring photographs appear in Figures 21 through 25.

The test results indicate the USG 14SC material to be superior to M50 tool steel in block and ring wear. The wear of the RC-2-lubricant mixture at room temperature is equivalent to the lubricant wear at 600°F. The lubricant wear is less at room temperature on the USG 14SC material than at 600°F, while the opposite seems true with M50. The 5% dilution of the lubricant with RC-1 has little effect on wear on the USG 14SC and M50 materials at room temperature. Besides showing high wear, the M50 tool steel wear characteristics indicate welding and scoring in the wear areas.

It is concluded that the combination of either candidate working fluid/eutectic/lubricant/cast iron/graphite is a workable one insofar as lubrication against sliding wear is concerned.

5.8.3 Special Lubricant Synthesis

A limited synthesis effort was undertaken in an attempt to find new lubricants stable at 720°F in the presence of the methylpyridine-water fluids, yet relatively poor solvents for the working fluid. Briefly the situation at the onset of this work could be summarized as follows. Only a few polyaromatic liquid oils are stable above 712°F in the presence of pyridine-water working fluids. All of these stable materials are good solvents for pyridine and the methylpyridines, and hence are extensively diluted by the working fluid and, in fact, barely form two phases at room temperature.

Table 35. RUB BLOCK WEAR TESTS OF LUBRICANT AND MIXTURES OF RC-1 and RC-2 WITH LUBRICANT

Test conditions:

Ring diameter = 1.5 in.
Block thickness = 0.25 in.
Ring speed = 3200 rpm

Test duration = 60 min.
Load between blocks and ring = 44.2 lb_f
Ring material = Cast iron[1]

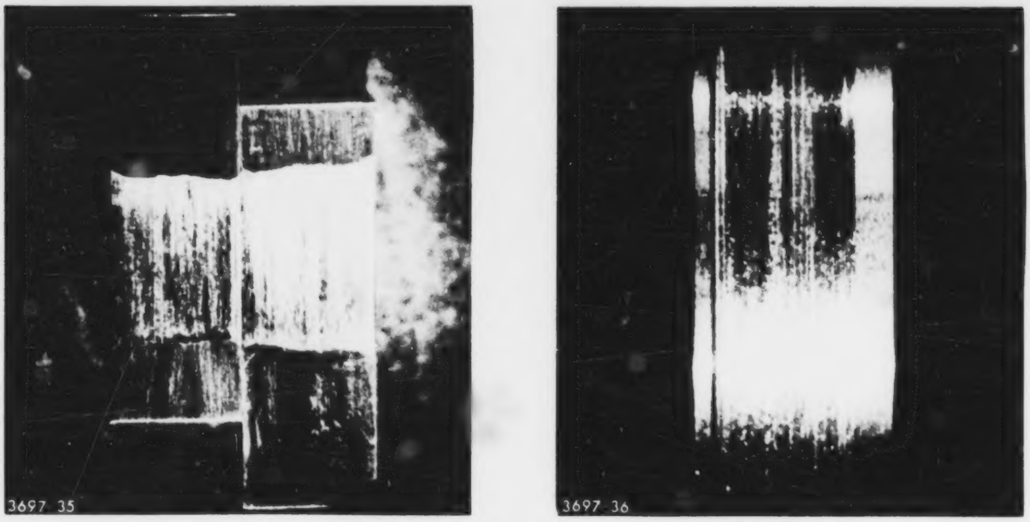
Test No.	Fluid	Fluid Temp (°F)	Block Material	Scar Width (in.)
7	Biphenyl-terphenyl Eutectic (lubricant)	600	US Graphite 14SC	0.083
8	Same	600	M50 Tool Steel[2]	0.225
9	Same	RT	M50 Tool Steel	0.323
10	Same	RT	US Graphite 14SC	0.058
11	50% wt. Lubricant 50% wt. Candidate RC-2	RT	US Graphite 14SC	0.081
12	Same	RT	M50 Tool Steel	0.112[3]
13	95% wt. Lubricant 5% wt. Candidate RC-1	RT	US Graphite 14SC	0.059
14	Same	RT	M50 Tool Steel	0.275
15	Suniso 3G Oil	RT	US Graphite 14SC	0.067
16	Same	RT	M50 Tool Steel	0.038

---

[1] Ford cast iron - Material ESE-MIA117-B

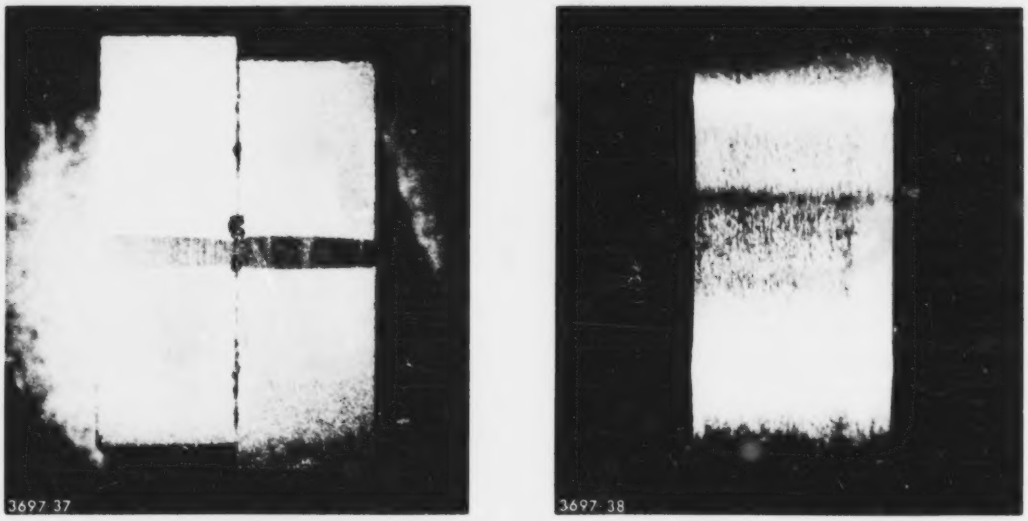
[2] Hardness = 60 RC, surface finish = 8μ-in. RMS

[3] Friction torque exceeds limit of torque cell, reduce load to 29.5 lb_f



22a. M50 Blocks 22b. Cast Iron Ring

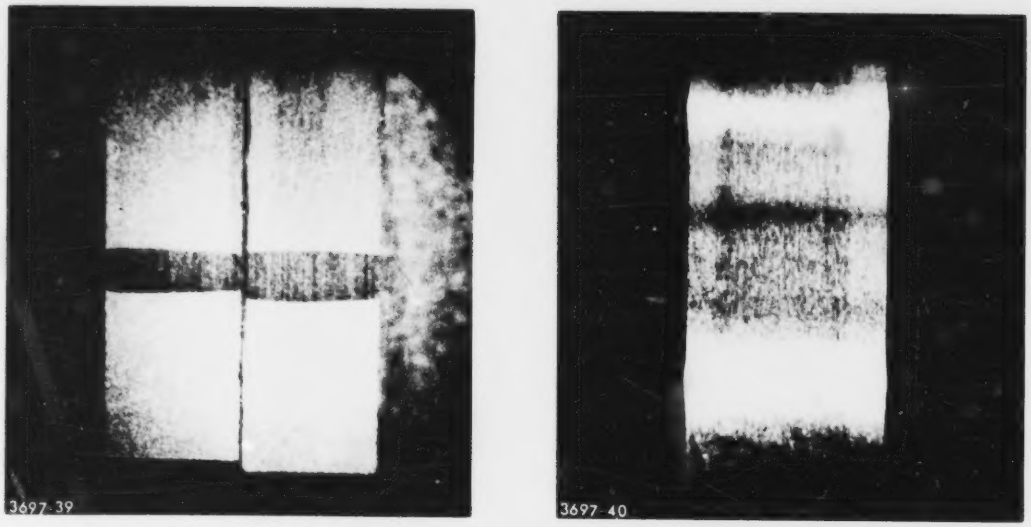
Test 9



22c. M50 Blocks 22d. Cast Iron Ring

Test 10

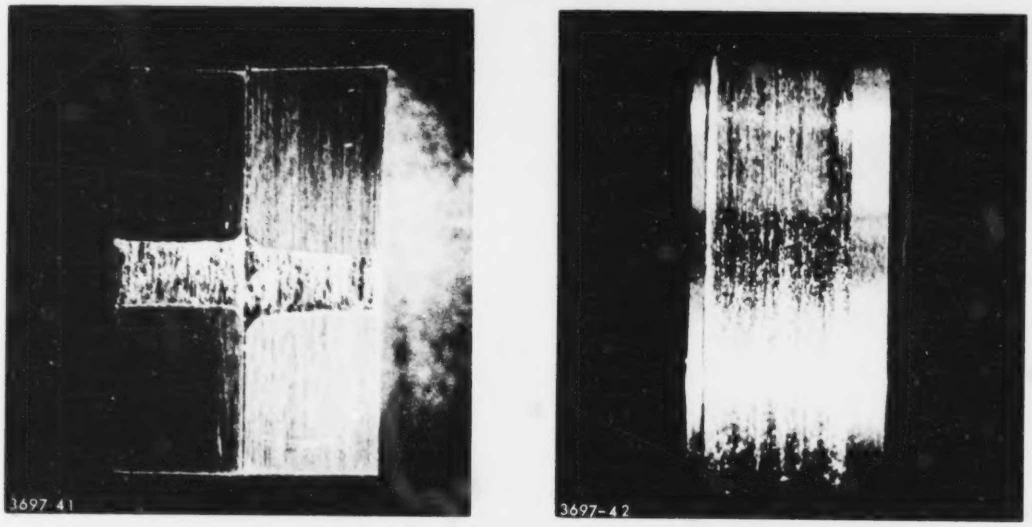
Figure 22. Rub Block Wear Specimens (3.2x)



23a. 1450 Blocks

23b. Cast Iron Ring

Test 11

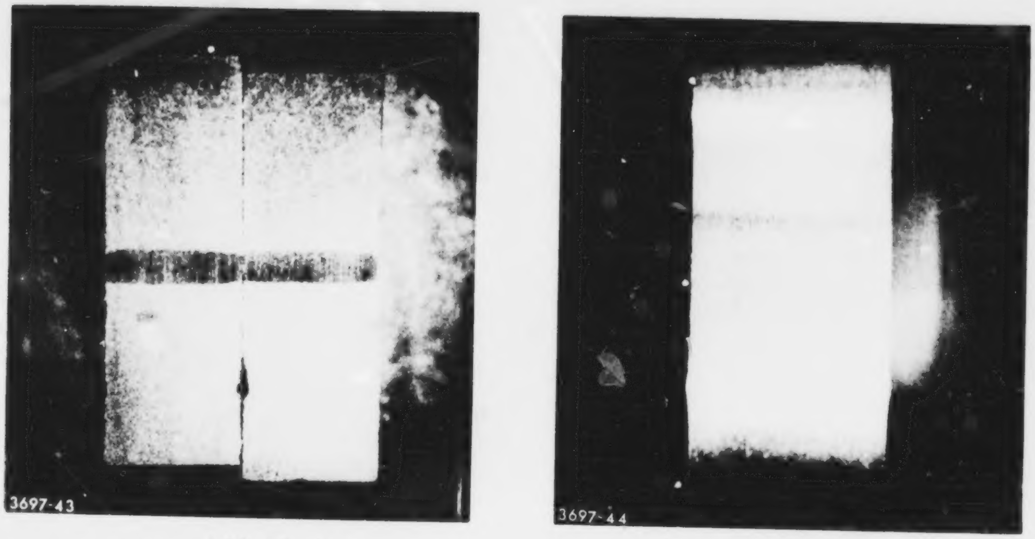


23c. M50 Blocks

23d. Cast Iron Ring

Test 12

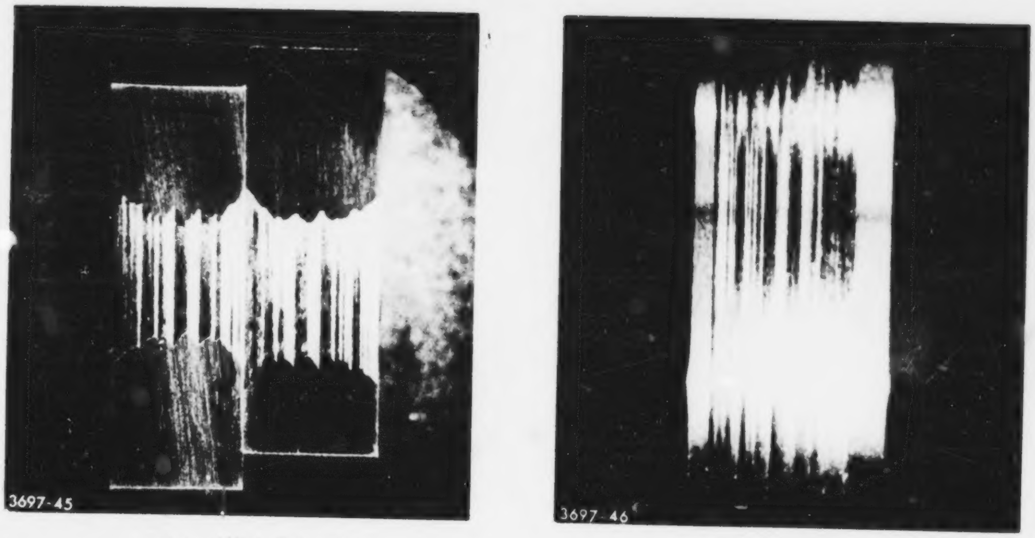
Figure 23. Rub Block Wear Specimens (3.2x)



4a. [illegible] Blocks

4b. Cast Iron Ring

Test 13

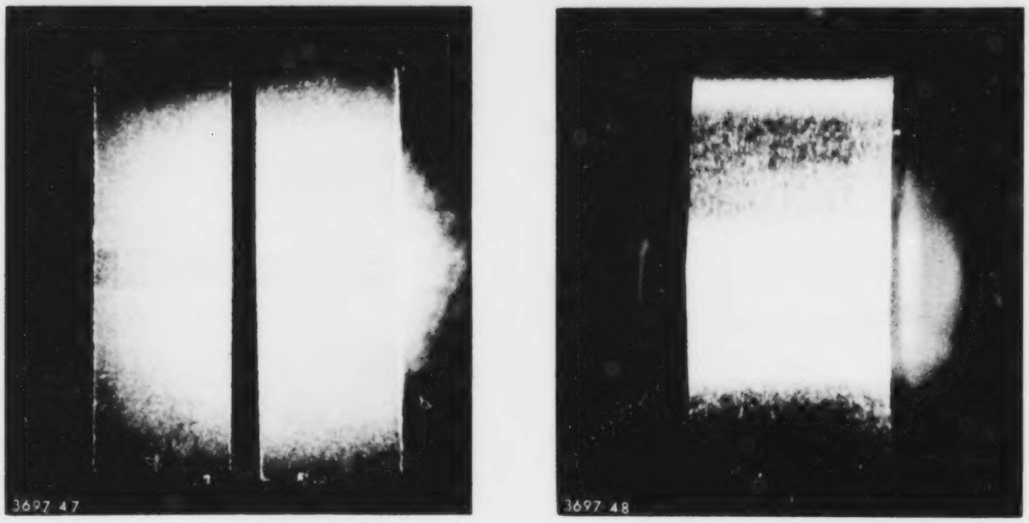


4c. [illegible] Blocks

4d. Cast Iron Ring

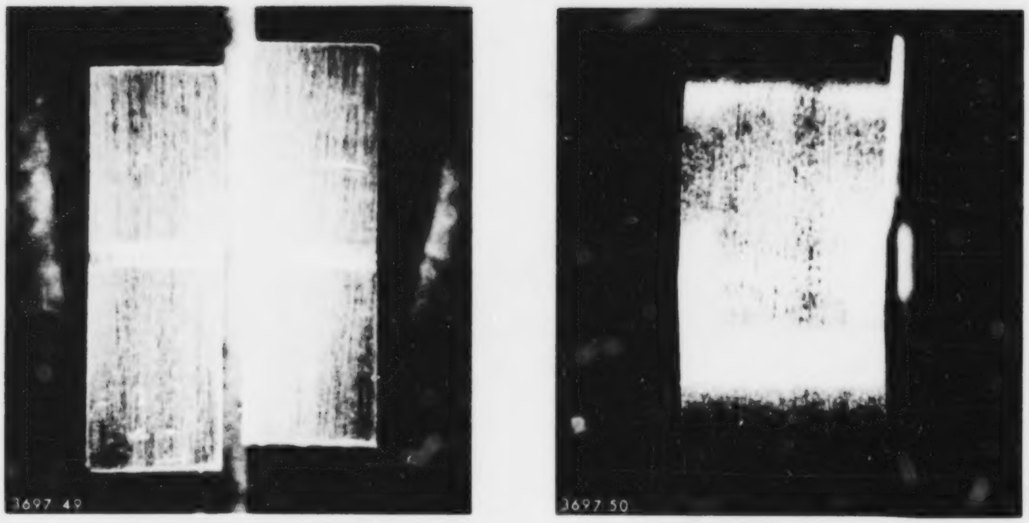
Test 14

Figure 24. Rub Block Wear Specimens (3.2x)



25a. [illegible] Blocks   25b. Cast Iron Ring

Test 15



25c. 450 Blocks   25d. Cast Iron Ring

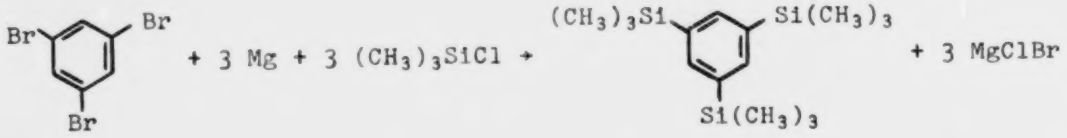
Test 16

Figure 25. Rub Block Wear Specimens (3.2x)

Oils which are primarily aliphatic in character (i.e. mineral oils similar to Suniso 3GS) appear to be sufficiently insoluble in the methylpyridine water fluids, but these materials are not thermally stable above about 660°F. Similarly, polyfluorinated kerosene or KRYTOX ethers are quite insoluble but are chemically unstable in the presence of the working fluids. One possible way to resolve this dilemma would be in the synthesis of a stable, largely aliphatic molecule. This approach was followed.

Advantage was taken of the fact that methyl-silicon bonds are abnormally stable. A trimethylsilyl group $(CH_3)_3Si$- is relatively large sterically and somewhat more thermally stable than a non-silicon-containing hydrocarbon group of comparable size. By attaching several trimethylsilyl groups to the benzene nucleus, it was hoped that a stable, low-solubility oil might be obtained.

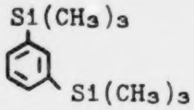
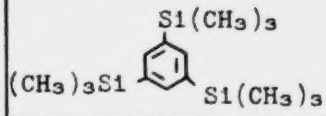
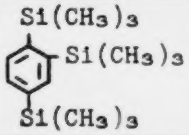
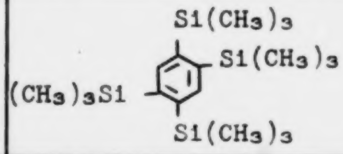
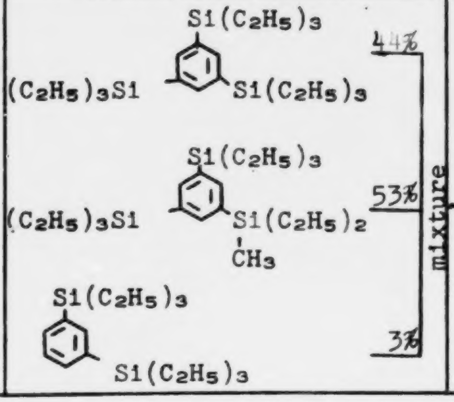
The method of synthesis was that employed by Chaffer and Beck (ref. 23) for the preparation of sym-tris (trimethylsilyl) benzene.



Two oils, 1,3-bis(trimethylsilyl)benzene and 1,3,5-tris(trimethylsilyl)benzene, were prepared. Equilibration with methylpyridine-water fluids showed that the trisilyl-substituted benzene was, indeed, a relatively poor solvent for 2-methylpyridine-water. In addition, ampoule tests indicated that both of the silylbenzenes were about as thermally stable as the methylpyridine-water working fluids, and were not chemically attacked by the latter. Thus a polytrimethylsilyl aromatic of suitable physical properties could conceivably be an acceptable immiscible lubricant for use with 2-methylpyridine-water. Difficulties arose, however, upon investigation of the low temperature properties of the two fluids when it was found that the trisilylbenzene crystallized at +81°F. Data on both 1,3-bis(trimethylsilyl)benzene and 1,3,5-tris(trimethylsilyl)benzene are summarized in Table 36. Here it can be seen that the melting points of the possible silane candidates are discouragingly high and even the use of mixed silanes (example #3) does not provide a -20°F flow point with the 2-methylpyridine working fluid.

In an effort to improve the situation, two additional trimethylsilyl-substituted benzenes, shown in Table 36 as examples 4 and 5, were prepared by procedures similar to the first two. These

Table 36. SOLUBILITIES AND LOW TEMPERATURE BEHAVIOR OF ARYL SILANE LUBRICANTS

Expt. No.	Silane	mp (°F) "Pure"	After Equilibration With RC-2	
			Flow Point (°F)	Solubility of 2-MP in Lube (Wt %)
1		+ 12	~-10	20
2		+ 81	~+30	14
3	50/50 mix of #1 & #2	--	~-10	17
4		+109	--	--
5		+333	--	--
6	50/50 mix of #2 & #4	+ 5	-13	14.2
7	 Si(C₂H₅)₃ (C₂H₅)₃Si Si(C₂H₅)₃ 44% Si(C₂H₅)₃ (C₂H₅)₃Si Si(C₂H₅)₂ CH₃ 53% mixture Si(C₂H₅)₃ Si(C₂H₅)₃ 3%	~- 76	~-103	11.3

compounds unfortunately had still higher melting points and thus appear to be useless for the intended application, although a mixture of the isomeric tris trimethylsilylbenzenes 2 and 4 (example 6 of Table 36) offered some encouragement.

In an effort to work around the crystallinity impasse the complex triethylsilylbenzene mixture shown in example 7 of Table 36 was prepared from 1,3,5-tribromobenzene and triethylchlorosilane. It was expected that the use of triethylsilyl groups in place of trimethylsilyl would drastically lower the melting points of the polysilylated benzenes and, indeed, this proved to be the case. Unfortunately the presence of the triethylsilyl groups, i.e. $(C_2H_5)_3Si$-, also appreciably lowered the thermal stability of the oil, so that ampoule tests at 720°F revealed extensive decomposition of the lubricant after 48 hours of exposure. No further attempts along these lines were made to define an immiscible lubricant.

Prospects for finding an immiscible lubricant for RC-2 are not considered bright. Lubricants possessing the necessary insolubility are mostly of chemical types which are not stable to 720°F. Best prospects seem to be in extending the silane work reported here, but ultimate costs of such materials would be high.

5.9 MANUFACTURE AND ECONOMICS

5.9.1 Final Candidate RC-1

Polyfluorobenzenes are currently custom-produced only in small amounts at high cost by the direct fluorination of benzene with cobalt trifluoride (ref. 24). While the process is well known and convenient for small scale production, it is too chemically inefficient to be seriously considered at the 50 million pound annual production rate needed to support the manufacture of a million Rankine automobiles a year. Before a reasonable estimate of the ultimate owner's cost for the RC-1 fluid can be made, it is, therefore, necessary to define a "most probable" process, based on available technology. The process of choice is the so-called halogen exchange.

5.9.1.1 Halogen Exchange Process - This process basically converts hexachlorobenzene into a series of chlorofluorobenzenes by a fluorine-for-chlorine exchange between hexachlorobenzene and a fluoride salt, as in the reaction:

$$C_6Cl_6 + nKF \rightarrow C_6Cl_{6-n}F_n + nKCl$$

In general, the reaction products are found to contain all possible combinations of chlorine and fluorine on the fully halogenated benzene ring. In other words, compounds represented by all values of n from 1 to 6 are simultaneously formed in the reaction.

The major ingredients of RC-1 are hexafluorobenzene (n=6) and pentafluorobenzene. The latter is not a direct product of the exchange reaction, but it is readily obtained from the n=5 product by hydrogenation:

$$C_6ClF_5 + H_2 \rightarrow C_6HF_5 + HCl$$

This reaction is quite selective in that the chlorine is replaced, but not the fluorine atoms.

Other products of the original exchange reaction, those with n=1 to 4, can be upgraded to a higher degree of fluorination (higher n) by simply being re-exposed to the exchange conditions of the initial reaction.

These reactions are the bases for the RC-1 plant conceived as depicted in the flow sheet of Figure 26. Recent patent literature (ref. 25-28) supplied much of the detail, but many assumptions were necessary to fill in gaps.

Referring to Figure 26, liquid hexachlorobenzene is pumped into the tubular substitution reactor at a pressure of about 560 psig. In the flue-gas-heated reactor, it travels through tubes packed with solid potassium fluoride. The halogen exchange reaction occurs at the solid-liquid interface at a temperature near 1000°F. On leaving the reactor, the product stream is depressurized and cooled to about 450°F prior to entering a distillation column.

In the fractional distillation column, the desired products (n=5,6) are separated from low-boiling by-products and from the higher boiling chlorofluorobenzenes (n=0 to 4). They are then lead to a hydrogenation reactor which selectively converts the chloropentafluorobenzene into pentafluorobenzene, leaving the hexafluorobenzene unaffected. Hydrogen is admitted to the reactor at a pressure of about 100 psig. The reaction takes place at a controlled liquid temperature of 300°F. Hydrogen chloride resulting from the hydrogenation reaction is recovered from the hydrogen atmosphere and sold or used elsewhere.

The liquid product from the hydrogenation step is the final RC-1 fluid. Ingredient ratio is controlled by the reaction conditions maintained in the halogen exchange reactor. Too high a ratio of C_6F_6 to C_6HF_5 can be corrected by reducing the dwell time or by altering other reaction conditions.

The high-boiling bottom fraction from the distillation, which contains primarily fluorine-lean compounds of $n<5$, is returned as recycle to the exchange reactor. These materials are thus re-exchanged to higher levels of fluorination, eventually to the

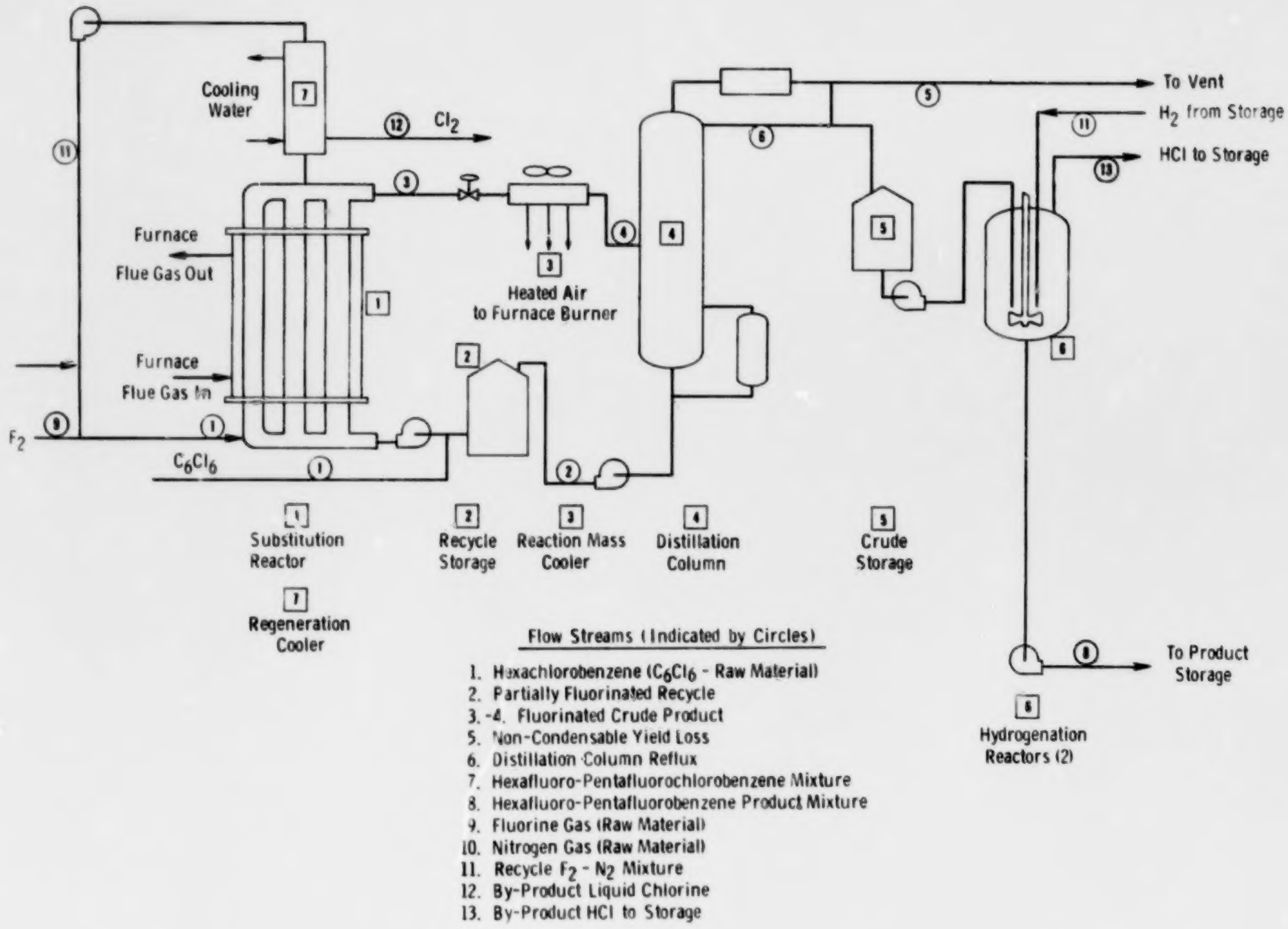

Cooling Water
7
12
Cl_2
11
Furnace Flue Gas Out
Furnace Flue Gas In
F_2
9
1
C_6Cl_6
1
3
1
Heated Air to Furnace Burner
3
4
4
2
2
6
5
To Vent
11
H_2 from Storage
13
HCl to Storage
5
6
8
To Product Storage
1 Substitution Reactor
7 Regeneration Cooler
2 Recycle Storage
3 Reaction Mass Cooler
4 Distillation Column
5 Crude Storage
6 Hydrogenation Reactors (2)
Flow Streams (Indicated by Circles)
1. Hexachlorobenzene (C_6Cl_6 - Raw Material)
2. Partially Fluorinated Recycle
3.-4. Fluorinated Crude Product
5. Non-Condensable Yield Loss
6. Distillation Column Reflux
7. Hexafluoro-Pentafluorochlorobenzene Mixture
8. Hexafluoro-Pentafluorobenzene Product Mixture
9. Fluorine Gas (Raw Material)
10. Nitrogen Gas (Raw Material)
11. Recycle F_2 - N_2 Mixture
12. By-Product Liquid Chlorine
13. By-Product HCl to Storage

Figure 26. Manufacture of Highly Fluorinated Benzenes (C_6F_6/C_6F_5H) KF Regeneration in Place

desired n=5,6 level. An occasional purge of high molecular weight polymeric residues (not shown in flow sheet) would be necessary to prevent their over-accumulation in the recycle loop.

The gradual conversion of the KF into KCl accompanying the exchange reaction slows the reaction to the extent that it must be periodically interrupted to allow the salt to be regenerated to the fluoride form. In the conceptual process, a make time of 12 hours was assumed. It was also assumed that at the end of the "make" portion of the cycle, half the original KF is converted to KCl. At this point, feed to the reactor is stopped and the reactor is vented to the distillation column. After cooling the reactor contents to the range 500-600°F by circulating nitrogen (N_2), fluorine (F_2) is admitted to the gas stream and a halogen exchange takes place which converts KCl back to KF with the generation of Cl_2. Cl_2 may be condensed from the mixed F_2-Cl_2-N_2 gas stream for sale as a by-product.

Following regeneration of the KF, the reactor is reheated to reaction temperature (1000°F), raw material and recycle streams are restarted, and the reaction proceeds again for another 12 hour period.

Major assumptions about the process are listed below:

A. Overall Material Balance

1) Onstream time would be 7500 hr/yr

2) A 40/60 molar split between C_6F_6/C_6F_5H is the optimum fluid of this type

3) Yields: F_2 90%
C_6Cl_6 95%

4) Plant design capacity - 50,000,000 lb/yr

B. Substitution Reactors

1) Retention time - 1/2 hr

NOTE: This sets the requirements of this reaction step at one reactor with 53 8 in. dia., 20-ft long tubes.

2) A total downtime for regeneration will be 4 hr

3) The reactivity of the fluoride salt will reach an unacceptable level after 12 hr running time.

C. Distillation Column

1) Atmospheric pressure
2) 10 theoretical trays are necessary
3) Minimum reflux ratio to achieve the split required is 1.7/1.
4) These parameters set specifications of the column at 3 ft dia. and 60 ft tall with 20 sieve trays.

D. Hydrogenation Reactor

1) Retention time will be 2 hr.
2) Total turnaround time will be 3 hr.
3) The size of the reaction system is then two 1500-gal. reactors.

5.9.1.2 Halogen Exchange Economics - Capital and operating costs were estimated for the hypothetical 50 million pound per year RC-1 plant described above. Because the technology of the process is very sketchy, the accuracies of the resulting estimates are not considered high enough to warrant a final decision on economic suitability of the fluid. The data are considered sufficiently accurate to support additional process research and development.

The estimate of capital requirements was made using equipment pricing factors, installation costs, and overhead factors from published correlations (ref. 29, 30) or from Monsanto's proprietary experience records, whichever was believed more reliable. All cost data were referred to 1972 using the Marshall and Stevens Equipment Cost Index. The "battery limits" capital estimate was $6,000,000. When support capital and working capital are added, the total capital investment is $37,000,000. This estimate is considered to have an accuracy of ±25.

In addition, and using a Monsanto-proprietary economic evaluation program (E0058), the cost of operating such a plant at capacity was estimated. Costs normally sensitive to the choice of site for plant construction were assumed at levels representing an "economically favorable U.S. location", without specifying where it might be. Other assumptions were made with the intent of producing a "moderately optimistic" analysis to define the likely lower bound on ultimate costs. Both the assumptions and resulting analysis are given in Tables 37 and 38.

The estimated bulk manufacturing cost of $1.00 per pound is considered the lowest probable cost after several years operating experience in a plant operating at full capacity.

Table 37. MANUFACTURING COST ESTIMATE - RC-1

HEXA-/PENTAFLUOROBENZENE - 50 MILLION POUNDS PER YEAR
YIELDS: ON FLUORINE = 90%. ON HEXACHLOROBENZENE = 95%
BY-PRODUCT CREDIT OF $0.015 PER LB CL2 AND $0.030 PER LB HCL

MANUFACTURING COST ESTIMATE

M&E	$M	5600	DESIGN RATE	50000000 LB/YR	7500 OPERATING HR/YR
BLDG	$M	400	PRODUCTION	50000000 LB/YR	100.0 % OF DESIGN
TOTAL	$M	6000			

	UNITS/YR OR %	UNIT OR % BASIS	$/UNIT	PRACTICE LB/LB	$M/YR	$/LB
MATERIALS						
C6CL6	85499936	LB	0.180	1.710	15390	0.308
F2	32499952	LB	1.000	0.650	32500	0.650
H2	400000	LB	1.000	0.008	400	0.008
N2	47949952	LB	0.020	0.959	959	0.019
CL2	-54599936	LB	0.015	-1.092	-819	-0.016
HCL	-6249999	LB	0.030	-0.125	-187	-0.004
TOTAL MATERIALS					48242	0.965
DIRECT EXPENSE						
LABOR	41600	MAN HRS	5.50		229	0.005
SUPERVISION	8320	MAN HRS	6.50		54	0.001
PAYROLL CHGS	25.0%	LABOR+SUPV			71	0.001
ELECTRICITY	27500	CKWH	1.500		41	0.001
PROCESS WATER	900	MGAL	0.200		0	0.000
FUEL GAS	60000	MMBTU	0.400		24	0.000
REPAIRS M&E	8.0%	M&E			448	0.009
REPAIRS BLDG	4.0%	BLDG			16	0.000
LABORATORY	1700	MAN HRS	10.000		17	0.000
CLOTH & LAUND	2.0%	LABOR+SUPV			6	0.000
FACT SUPPLIES					30	0.001
TOTAL DIR EXP					936	0.019
INDIRECT EXPENSE						
DEPR M&E	10.0%	M&E			560	0.011
DEPR BLDG	4.0%	BLDG			16	0.000
FIE - NON-CONT	1.5%	M&E+BLDG			90	0.002
FIE-CONTROLLABLE					183	0.004
TOTAL IND EXP					849	0.017
TOTAL CONV COST					1784	0.036
BULK MFG COST					50027	1.001
TOTAL FOR COST OF GOODS					50027	1.001

Table 38. RETURN ON INVESTMENT - RC-1

```
HEXA-/PENTAFLUOROBENZENE  -  50 MILLION POUNDS PER YEAR
YIELDS:  ON FLUORINE = 90%,  ON HEXACHLOROBENZENE = 95%
BY-PRODUCT CREDIT OF $0.015 PER LB CL2 AND $0.030 PER LB HCL

                  R E T U R N   O N   I N V E S T M E N T

 DESIGN RATE   50000000 LB/YR            PRODUCTION   50000000 LB/YR


                        EARNINGS SUMMARY                           $M/YR

ANNUAL GROSS SALES @    1.398 $ PER LB                             69923

ANNUAL NET SALES                                                   69923
   LESS FOR COST OF GOODS SOLD                                     50027

GROSS PROFIT                                                       19896
   LESS MAT  EXPENSES @ 10.00 % OF SALES                            6992
   LESS CORP INVEST CHG @  5.00 % OF NET INVESTMENT                 1590

INCOME BEFORE TAX                                                  11315
   LESS INCOME TAX @ 50.00% OF INCOME BEFORE TAX                    5657

NET INCOME                                                          5657


                        CAPITAL SUMMARY                               $M

NEW FIXED CAPITAL                                                   6000
   ALLOCATED UTILITY AND SERVICE CAPITAL                             945
   ALLOCATED MAT  CAPITAL                                           4895

TOTAL FIXED CAPITAL                                                11840
   WORKING CAPITAL @ 37.00 % OF SALES                              25872

GROSS INVESTMENT                                                   37712


                               ROI

ANNUAL RETURN ON INVESTMENT AFTER TAXES    15.00 %
```

Of the various elements contributing to this cost, the raw materials at $0.97 per pound dominate. Obviously, any appreciable reduction in the cost can only be achieved by significant improvement in yields or significant reductions in raw material costs. Yields on both hexachlorobenzene and fluorine were assumed above 90%, so there is not much improvement possible in these respects. The assumed fluorine cost of $1.00 per pound (ref. 31) was verified in consultation with Allied Chemical Corporation and is based on a price-volume extrapolation to quantities involved in an automotive market. This price is considerably below present prices, by a factor of about four. It is unrealistic to expect a more favorable price.

Fluorine is, however, available in a cheaper form than the assumed elemental liquid (for example, in combination with other elements in the minerals fluorspar and cryollite). Perhaps the best hope for ultimately lower prices lies in the invention of a way to exploit a cheap inorganic fluorine compound without going through the expensive elemental form.

Turning to the return on investment analysis of Table 38, the FOB plant selling price is next estimated at $1.40 per pound after assuming a 15% return on gross investment and applying typical factors for marketing, administration and technical expenses, and for income taxes and debt service. The gross investment, in turn, was calculated from the earlier estimate of new fixed capital by the use of typical factors for allocated capital and working capital.

As with the bulk manufacturing cost, the bulk FOB price is considered a minimum after several years of full production. It could legitimately be argued that a 15% return on investment is insufficient incentive to interest most potential manufacturers in a venture as technically and economically speculative as the one at hand. A substantial and successful technical and commercial development, underwritten by funds not included in this economic assessment, is considered a likely prerequisite.

The estimated $1.40 per pound FOB bulk sales price may be translated into a 5-year automobile owner's cost of $112 by entering Equation 21 (section 6.1.3) with the defendable assumption that no fluid replacement would be needed in the 5-year period. A basic assumption in the calculation was that the fluid charge is 40 pounds (equivalent to 3 gallons liquid).

While this projected owner's cost exceeds the goal of $100, it is close enough to warrant the acceptance of RC-1 as a final fluid candidate on the strength of its more positive attributes.

5.9.2 Final Candidate RC-2

Both the water and the 2-methylpyridine components of this candidate are currently available in commercial quantities. Water, even in the highly purified form demanded in this application, can be obtained for less then 1¢ per pound (ref. 32). The cost of the water per pound of working fluid would, therefore, be less than 0.4¢ per pound, which is negligible compared to the cost of the 2-methylpyridine.

5.9.2.1 2-Methylpyridine Technology and Economics - Most currently-produced 2-methylpyridine (or α-picoline) comes from the distillation of coal tar resulting from the manufacture of metallurgical coke from coal. The current U.S. market for this material is not large, being less than four million pounds per year. The amount available at any particular time is obviously tied to the simultaneous rate of steel production. The current market price of the coal-tar derived material is 47¢ per pound in tank car lots.

When supplies from coal tar sources are not adequate, 2-methylpyridine is available as a by-product from the synthesis of pyridine. This technology is practiced by Reilly Tar and Chemical Company of Indianapolis, Indiana, and others. The process is a vapor phase catalytic reaction which converts acetaldehyde and ammonia into pyridine and 2-methylpyridine in a mole ratio of about 1.0/0.6. What product is not sold on the open market is converted internally to vinyl pyridine and niacin. The market price of the synthetic 2-methylpyridine is currently 60¢ per pound in drum lots (ref. 33). Its purity is somewhat higher than that of the coal-tar-derived material.

Although the raw materials, acetaldehyde and ammonia, are available in plentiful supply, the current installed capacity for synthesizing 2-methylpyridine would not accommodate the demand from a million vehicle per year automotive market. Facility expansion and process modifications would undoubtedly be required. U.S. Patent 2,698,849 (ref. 34) teaches that acetaldehyde and ammonia exposed to a silica-alumina-thoria catalyst in the vapor phase at 450°C will result in a product consisting mainly of 2-methylpyridine and 4-methylpyridine. Technology of this type could be exploited to meet a large demand for picolines. It is likely that, with technological development, the selectivity of this or similar processes could be improved in the direction of the 2-methylpyridine. Furthermore, as noted in the specification of composition of RC-2 of Section 5.1.2, 4-methylpyridine is considered a valid co-ingredient. It is thus reasonable to expect that the picoline technology would quickly adapt under the competitive economic pressures of a developing automotive market to supply the methylpyridines needed at prices quite near the current prices. By-product imbalances would not likely be severe or long-lived.

5.9.2.2 RC-2 Cost - Based upon current prices and projected demands, it is reasonable to assume that Rankine-grade RC-2 could be purchased in bulk, FOB producer, for 55¢ per pound. This tacitly assumes reestablishment of coproduct market equilibrium after the upsetting influence of a sudden demand for 2-methylpyridine. Assuming, as before, a 3-gallon per vehicle charge, and noting that the density of the fluid is very near that of water, it follows from Equation 21 of Section 6.1.3 that the original vehicle fill plus three refills over the 5-year car life would cost only a few cents over the $100 limitation. At this rate, each charge of fluid would experience something like 400 hours of hot usage. This seems a very conservative usage provided a suitable material of high temperature system construction is used.

6. THE SEARCH

An ability to recognize one prospect among a host of possible choices is the key to a wide-ranging search for new automotive working fluids. Known pure chemical species number in the millions. Since mixtures of pure species are permissible, the possible choices are truly infinite. A rationale for accepting or rejecting specific materials at several levels of familiarity was clearly required to meet contract goals.

Table 39 lists the various characteristics desired of the working fluid and those characteristics of the propulsion system impacting on fluid choice. These were gleaned primarily from the contract scope of work, given in Appendix A, and from EPA vehicle design goals (ref. 35). Using these goals, a set of selection criteria were established to guide the search for new fluids.

6.1 SELECTION CRITERIA

An idea for a new fluid is normally a mental image of its chemical structure. Given such an image, it is a simple matter to check the chemical literature and learn whether the compound is known. If it is, the chances are good that its melting and boiling points are reported, but not much else of great help. Melting point, boiling point, and chemical structure thus are core data upon which a first judgment of suitability may be based. A set of screening criteria cover this level.

Experiment and computation are normally needed to further expand knowledge of candidate suitability. These are the main approaches employed in the later criteria covering cycle utility. Safety, cost, compatibility and lubricant selection are handled on an ad hoc basis with the advanced candidates only. Fluid cost criteria were originally established but were later abandoned when found untrustworthy.

6.1.1 Screening Criteria

6.1.1.1 Criterion 1. Known and Available - The contract requirement of a search for existing fluids is interpreted to restrict the search to fluids which are quantified combinations of known chemical compounds, each of which is recorded in the open literature and obtainable in multi-gram amounts at reasonable expense without being synthesized by the contractor (except as a last resort). This rules out fluids which are ill-defined, secret, hypothetical, unavailable, or very expensive.

6.1.1.2 Criterion 2. Melting Point Below 20°C (68°F) - The working fluid must obviously be fully liquid at the lowest required normal-start ambient temperature of -20°F (-29°C) and either fully liquid or non-damaging to the engine down to the

Table 39. PROPULSION SYSTEM AND WORKING FLUID GOALS

Propulsion System Characteristic	Goal[1]
Type Expander	1-stage recip. and 1-stage turbine
Approx. Net[2] Full Power	145[3] HP
Max. Weight	1600 lb
Max. Volume	35 cu ft
Regenerator Size	Nil or small
Min. WF[6] Condensing Temp.	220°F
Max. Low Ambient Temp.	-40°F
Min. High Ambient Temp.	125°F
Max. Starting Time (idle at -20°F.	25 sec
Max. Starting Time (65% power) @ 60°F.	45 sec
Average Annual Usage	350 hr
Life Expectancy	3500 hr
Working Fluid Characteristic	**Goal[4]**
Presently available?	Yes
Min. Carnot Cycle Efficiency	42%
Min. Ideal Cycle Efficiency	30%
Max. Cost[5] to Owner, 5 yr. period	$100
Compatible with Low Cost Materials?	Yes
Compatible Lubricant Needed?	Yes - recip. Maybe - turbine
Health Hazard	Nil
Fire and Explosion Hazard	Nil
Environmental Hazard	Nil

NOTES:

1. Prime sources: 1971 Vehicle Design Goals (EPA) as amplified in consultation with EPA
2. Gross expander shaft less feed pump shaft
3. Sundstrand calculation based on performance requirements of 1971 Vehicle Design Goals (EPA)
4. Prime source: contract work statement
5. Initial factory fill plus materials only for any subsequent refills
6. "Working Fluid"

lowest specified ambient temperature of -40°F (-40°C). To qualify as a working fluid, a pure compound must, therefore, have a melting point of or below -29°C. This restriction does not apply to the individual components of a mixed fluid, because the liquidus or crystallizing point of a solution is often many degrees lower than the melting point of the highest melting ingredient. The ability of one compound to depress the crystallizing point of another varies widely, so the selection of the particular value of 20°C is somewhat arbitrary. It is understood that compounds having melting points between -29 and 20°C are only to be considered potential components of a mixed fluid of suitably low crystallizing point. The term "flow point" has been adopted to encompass the behavior of either simple or complex fluids. It is the lowest temperature at which the fluid flows freely.

6.1.1.3 Criterion 3.
Normal Boiling Point 65 to 120°C (150-250°F) - The vapor pressure characteristic of the working fluid determines the pressure to be encountered wherever liquid and vapor coexist at a particular temperature. It is particularly important that the condensing pressure is within reasonable limits. Too high a pressure requires a condenser so heavy, bulky, or expensive as to be impractical. Too low a pressure leads to excessive pressure drops in the vapor passages, and poses difficulties in providing sufficient net positive suction head to avoid feed pump cavitation. Inleakage of air or outleakage of working fluid through shaft seals is more likely the farther removed the condensing pressure is from atmospheric. Reasonable condensing pressure limits were taken to be 5 to 50 psia at the advice of Thermo Electron Corporation system design engineers.

By plotting lines of typical slopes through the two limiting points (5 psia, 220°F and 50 psia, 220°F) on a log-pressure reciprocal-temperature chart, it was found that a normal boiling point range of 150 to 250°F could be expected to differentiate well those fluids meeting the 5 to 50 psia pressure limit.

6.1.1.4 Criterion 4. Thermally Stable at 720°F (382°C) - The requirement of a Carnot efficiency of at least 42%, coupled with a lowest allowed condensing temperature of 220°F, leads to the determination of the lowest high temperature of 712°F:

$$\eta_c = \frac{T_H - T_L}{T_H} \geq 0.42 \qquad (6)$$

$$T_L \geq 460 + 220 = 680°R \qquad (7)$$

$$T_H \geq 1172°R \equiv 712°F \qquad (8)$$

A working fluid meeting the Carnot efficiency requirement must, therefore, be reasonably stable in an engine environment when heated to a maximum bulk temperature of at least 712°F (preferably higher). For the purpose of a test definition, this temperature was rounded off at 720°F.

The screening criterion used to qualify a candidate under the Carnot efficiency requirement was as follows: the fluid must survive 200 or more hours of exposure in a steel ampoule held at 720°F without serious distress. Details of the test and the interpretations are given in section 6.3.

In arriving at the choice of 720°F for 200 hours as the test criterion, note was taken of the fact that in a flame-heated dynamic system the working fluid is exposed to temperatures considerably above and below the peak bulk temperature of the fluid leaving the vapor generator. The highest such temperature, called the hot-spot temperature, is a metal skin temperature somewhere near the exit of the vapor generator. Depending upon design and operating factors, it may be several tens to several hundreds of degrees Fahrenheit above peak fluid bulk temperature. Hot-spot temperatures are quite difficult to predict or measure accurately; they are therefore of severely limited utility in considerations of fluid life. Even though it is at the hot-spot where fluid decomposition is most rapid, the fact that only a very thin layer of fluid sees the temperature suggests that a system-overall decomposition rate is more readily related to a temperature near peak bulk. In any event, the selection of ampoule time-temperature conditions is arbitrary but nevertheless useful in distinguishing between stable and unstable fluids.

6.1.1.5 Regeneration and I-Factor - Compared to an internal combustion engine of the same power rating, the Rankine engine is inherently bulkier, primarily because it uniquely requires the transfer of large amounts of heat across solid-fluid interfaces. Heat exchangers peculiar to the Rankine engine are:

vapor generator

regenerator

condenser

While the automotive Rankine condenser seems comparable to the familiar radiator, it is required to reject many times more heat. In the conventional internal combustion engine, the major portion of the energy loss is through the high temperature exhaust gases, whereas in the Rankine engine the primary energy loss is in heat rejected to the ambient air in the condensing process.

The requirement that the Rankine engine fit in an engine compartment designed to house an internal combustion engine places severe restrictions on component size, and makes it very attractive to reduce or eliminate heat exchange components.

The regenerator, the only such component whose size or existence is sensitive to the choice of working fluid, has the sole function of recovering superheat from the engine exhaust to keep the cycle efficiency as high as practical. By judicious selection of working fluid and cycle operating condition, it is possible to arrange that the engine exhaust be at or near the saturated vapor curve and thus in need of little or no regeneration.

It is not difficult to conclude that an automotive regenerator is "too big" to fit in the engine compartment with the rest of the propulsion system if it occupies more than about 1.5 cubic feet of the approximately 30 cubic feet in the compartment. But this knowledge is of little help in screening many fluids because of the impracticality of performing the detailed system design analysis required to fix the regenerator size for each fluid. Therefore a parameter characteristic of the fluid and expressing the tendency of the isentropically expanding vapor to converge or diverge with the saturated vapor line was chosen as a screening parameter. This is the so-called I-factor.

6.1.1.6 Definition and Calculation of I-Factor - The enthalpy form of the thermodynamic equation of state for a closed uniform system is:

$$dH = TdS + VdP \qquad (9)$$

where H = enthalpy

T = absolute temperature

S = entropy

V = volume

P = absolute pressure

and the enthalpy change in terms of temperature and pressure differentials is:

$$dH = C_p dT + \alpha\, dP \qquad (10)$$

where $\alpha = (\partial H/\partial P)_T$

C_p = heat capacity at constant pressure

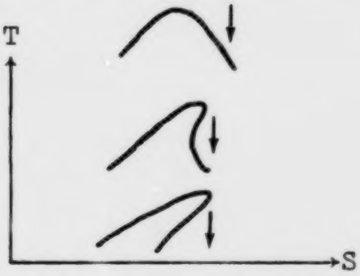
Combining these two expressions, while restricting them to the saturated vapor path (or dew line, subscript D), yields:

$$\frac{dT}{dS_D} = \frac{T/C_p}{1 - \left(\frac{V-\alpha}{C_p}\right) \frac{dP_D}{dT}} \qquad (11)$$

This expresses the slope of the dew line on a conventional temperature-entropy diagram in terms of the saturated vapor volume and specific heat and the dew pressure derivative. Direct use of this slope is not convenient because it acquires an infinite value and changes sign right in the middle of the most interesting region, i.e. where the line is near vertical. Also, it is desirable to use dimensionless quantities when comparing different fluids. For these reasons, the I-factor is defined as a dimensionless function of the slope as follows:

$$I(T) = 1 - \frac{T/C_p}{dT/dS_D} \tag{12}$$

With this definition, and considering a point on the dew line near the proposed condensing temperature but far below the critical temperature, the following conventions are valid:

TS Dome Shape	Fluid Isentropic Expansion Characteristic	Dew Line Slope	I-Factor
	Condensing	<0	>1
	Saturating	∞-	1+
	Superheating	>0	<1

Other authors have called these expansion characteristics wetting, isentropic, and drying, respectively.

Comparison of Equations 11 and 12 gives the basic relation for calculating I-factor:

$$I = \left(\frac{V-\alpha}{C_p}\right) \frac{dP_D}{dT} \tag{13}$$

$$\approx \frac{V}{C_p} \cdot \frac{dP_D}{dT} \tag{14}$$

The approximate form, fully valid where the saturated vapor behaves as a perfect gas, is intended for use only at temperatures (and pressures) far below critical. An alternate computational form is obtained when the Clapeyron equation

$$\frac{dP_D}{dT} = \frac{\Delta H_{BD}}{T\Delta V_{BD}} \qquad (15)$$

is substituted in Equation 13, giving:

$$I = \left(\frac{V_D-\alpha}{V_D-V_B}\right)\frac{\Delta H_{BD}}{CpT} \qquad (16)$$

$$\approx \frac{\Delta H_{BD}}{CpT} \qquad (17)$$

In these equations, the B subscript refers to the saturated liquid or bubble line. The approximation is good far from the critical temperature where both α and the saturated liquid specific volume, V_B, are negligibly small compared to the saturated vapor specific volume, V_D. Far from the critical temperature the enthalpy change of evaporation, ΔH_{BD}, and the specific heat Cp, of the saturated vapor are relatively constant, so the I-factor is nearly inversely proportional to absolute temperature over modest intervals.

6.1.1.7 Criterion 5. I-Factor Between 0.65 and 1.5 - The upper and lower limits on I-factor were chosen somewhat arbitrarily, but with the knowledge that ideal cycle efficiency must inevitably deteriorate rapidly as values of the I-factor deviate widely from unity.

Subsequent comparisons of real cycle efficiencies with I-factors for a number of working fluids have tended to confirm the suitability of the stated limits.

6.1.2 Cycle Criteria

Beyond the five screening criteria, it is important that a working fluid perform well in the particular Rankine cycle selected for it. Cycle efficiency, for example, is dependent upon the cycle selected as well as the thermodynamics of the fluid. It is thus necessary to select and define reference cycles before setting forth cycle criteria. Two such cycles are defined: the "reference ideal" and the "equivalent real" Rankine cycles.

6.1.2.1 Reference Ideal Cycle - Like any simple ideal Rankine cycle, the reference ideal cycle appears as a clockwise rectangle on a pressure-entropy diagram. On a temperature-entropy diagram, its trace is typified by cycle 123451 (solid line) of Figure 27. Vapor expansion and liquid compression are ideally reversible adiabatic processes, and, therefore, isentropic. Cooling and condensing occur at a constant low pressure P_4 over the path 234. Heating, which includes boiling and superheating in subcritical cycles, occurs along path 51 at a constant high pressure P_1. To

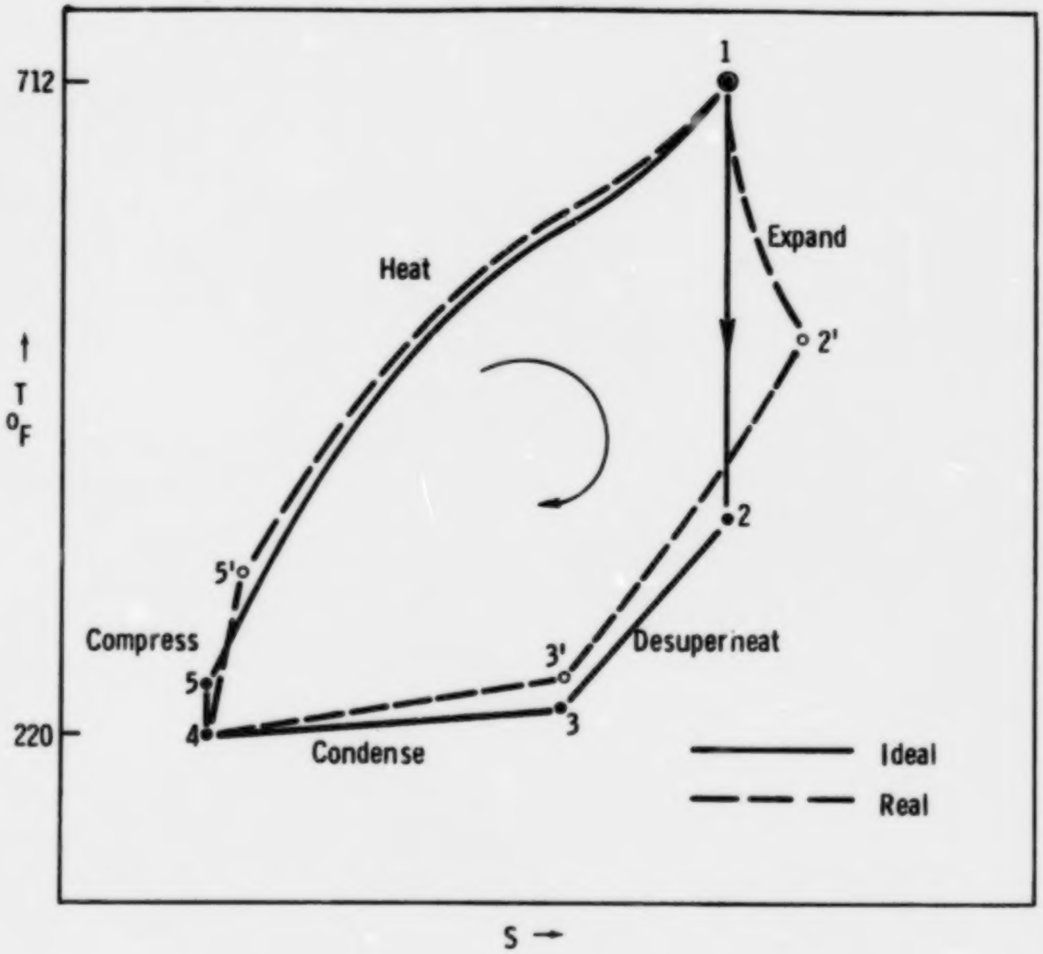


Figure 27. Reference Ideal and Equivalent Real Rankine Cycles

meet the 42% Carnot efficiency and the 220°F condensing temperature requirements, the extreme cycle temperatures are 712°F and 220°F at cycle "corners" 1 and 4, respectively. Finally, the two pressures are fixed by these conventions:

1. Point 4 is on the saturated liquid (or bubble) line; therefore, P_4 is the bubble point pressure at 220°F.
2. The pressure at point 1, P_1, is the lesser of:
   a) that pressure just preventing line 12 from penetrating the saturated vapor (or dew) line, or
   b) 1000 psia.

The rationale behind the second convention is as follows. Given a particular fluid, the effect of raising P_1 at fixed T_1 and P_4 is to increase the ideal cycle efficiency. There are, however, two limitations. One is that P_1 not exceed a practical upper limit where pump design, cost and reliability become problems, or where the safety of the occupants of the vehicle may be unduly threatened. This limit was placed at 1000 psia at the expander inlet to include the design pressures of the several system contractors. The other limitation is on the incursion of the expansion line into the two-phase region of the fluid. While both the turbine and reciprocating expanders can tolerate some expansion condensation, normal practice seems to be to design system hardware in the expectation that condensation will rarely, if ever, occur. For this reason, it was decided that the ideal expansion line on the T-S diagram should at no point penetrate the saturated vapor (or dew line) curve.

6.1.2.2 Equivalent Real Cycle - The "equivalent real" cycle is a hypothetical cycle associated intimately with the "reference ideal" cycle, while also being a much closer approximation of the intended prototype hardware cycle. Because it is closer to reality than the reference ideal cycle, it is of greater utility in evaluating and comparing working fluids.

The equivalent real cycle is illustrated by cycle $12'3'45'1$ in Figure 27 and is defined as follows:

1. Cycle corners 1 and 4 are identical to those of the reference ideal cycle (i.e., expander and pump inlet conditions are identical in the two cycles)
2. Principal irreversibilities, expressed as expander and pump efficiencies and as component pressure drops, were fixed after comparing the values being assumed by system designers at Thermo Electron Corporation and Aerojet Liquid Rocket Company in January 1972 as follows:

	Equiv. Real Cycle	Jan '72 Design	
		TECO	Aerojet
Expander Efficiency, %	75	75	74
Regen. Press. Loss, psi			
Vapor side	$0.09\ P_4$	$0.09\ P_4$	$0.00\ P_4$
Liquid side	$0.05\ P_1$	$0.01\ P_1$	$0.10\ P_1$
Cond. Press. Loss, psi	$0.14\ P_4$	$0.14\ P_4$	$0.00\ P_4$
Pump Efficiency, %	75	85	70
Vap. Gen. Press. Loss, psi	$0.10\ P_1$	$0.17\ P_1$	$0.025\ P_1$

3. Expander and pump are assumed to be adiabatic; thus the enthalpy change through either component is the negative of the work done on the surroundings.

6.1.2.3 Cycle Efficiency and Regeneration - Whether ideal or real, Rankine cycle efficiency is defined as follows:

$$\eta_{cyc} = \frac{\text{Net indicated work out}}{\text{Net indicated heat in}}$$

where net indicated work out is the algebraic sum of the enthalpy changes across the expander and the pump (with appropriate sign change), and net indicated heat in is the enthalpy rise across the vapor generator only. Note that whatever heat is added to the liquid by the regenerator reduces the amount of heat required from outside sources and thus increases the cycle efficiency. Any development of cycle efficiency criteria thus requires a simultaneous development of regeneration criteria.

The heat transfer rate in a regenerator is given as:

$$Q = UA\Delta T_m \tag{18}$$

$$= UAk\Delta T_{lm} \tag{19}$$

where Q = heat flow, energy/time

U = overall heat transfer coefficient, energy/time-area-temp.

A = interfacial area

ΔT_m = mean temperature difference, vapor to liquid sides

ΔT_{lm} = logarithmic mean temperature difference, vapor to liquid side

k = cross flow factor

As shown in heat transfer texts (e.g. ref. 36) the logarithmic mean temperature difference is the "correct" mean temperature difference to use when the exchanger is truly countercurrent. That is, $k = 1$ for simple counterflow. Other flow conditions, including multi-pass and cross flows are accommodated empirically by values of the multiplier k less than one.

Rearrangement of the heat transfer equation gives

$$UAk = Q/\Delta T_{lm} \qquad (20)$$

either side of which is a measure of regenerator "size". While UAk is not a direct measure of regenerator bulk, it is certainly well-correlated with bulk through its sensitivity to exchanger surface area, and is therefore useful as a size criterion. Obviously UAk follows the regenerator bulk by increasing when a) more heat must be transferred at constant ΔT_{lm}, or b) the same amount of heat must be transported at a lower ΔT_{lm}. Implicit here is the notion that comparisons are made between fluids having not too disparate thermal properties and at nearly equal pressure drops. In summary, then, the UAk product is selected as a useful, if imperfect, indicator of regenerator size and as a suitable basis for a criterion intermediate between the I-factor limits of Criterion 5 and the ultimate test of reasonableness provided by the system analysis, wherein actual optimum regenerator dimensions are generated.

Regenerator duty is conveniently expressed as its "effectiveness", which is that percent or fraction of the ultimately recoverable heat which is actually recovered. The ultimately recoverable heat is that theoretically recoverable in a pure counterflow regenerator of infinite area. Depending upon the relative heat capacities of the vapor and liquid streams entering the regenerator, 100% effective recovery implies stream temperature equality (zero ΔT) at one end or the other, usually at the vapor-out end.

6.1.2.4 Criterion 6. Reference Ideal Cycle Efficiency at Least 30% when UAk $\geq \infty$ - A 30% ideal cycle efficiency is required of the working fluid irrespective of the extent of regeneration. In testing a working fluid under this requirement, it is not instructive to limit the regenerator "size" (i.e. the UAk product) because regenerator size is strongly sensitive to expander exhaust fluid condition and to fluid flow rate, which variables are likely to be much different in a real (irreversible) cycle. This disparity, in fact, was the stimulus for the definition of the equivalent real cycle and the limitation of its regenerator size.

6.1.2.5 Criterion 7. Equivalent Real Cycle Efficiency when UAk = 125 Btu/HP-hr-F: Report (not limited) - The assignment of the particular UAk product of this criterion drew on prototype system designs of Thermo Electron Corporation and Aerojet

Liquid Rocket Company as existing in January 1972 and shown in Table 40.

Table 40. REGENERATOR DATA PRESENTED AT JANUARY 1972 CONTRACTORS' COORDINATION MEETING

	TECO	Aerojet
Working fluid	F-85	AEF78
Expander type	Recip.	Turbine
Net cycle horsepower	138	154
Regenerator Q, kBtu/hr	414	1300
Temperatures, °F		
Vapor in	376	480
Vapor out	248	230
Liquid in	214	170
Liquid out	283	400
Difference, Log.-Mean	59.4	69.5
Regenerator UAk*, Btu/HP-hr-F	50.5	121.4
Effectiveness, %	79	81
Regenerator size		
Dimensions, inches	27x8x7	2(20x10x6)
Volume, cubic feet	0.85	1.39

---

*Per net cycle horsepower

The table data demonstrate the type of correlation between UAk and regenerator volume alluded to earlier. In both cases, but especially in the Aerojet design, the regenerator size shown was thought to approach the maximum tolerable in the space available. Thus the criterion value of 125 represents a "tight fit" with a turbine system, and is likely a bit "oversized" for use with the somewhat bulkier reciprocating expander.

No specific contractual limit was imposed on permissible values of this criterion.

6.1.2.6 Criterion 8. Isentropic Expansion Enthalpy Drop $\overline{<}$ 200 Btu/lb (Turbine Engine Only - Equivalent Real Cycle) - The only organic-powered turbine expander under consideration by the Rankine system contractors during this study was the single-stage impulse type. In this type the working fluid is expanded virtually to expander exhaust pressure in a single convergingdiverging nozzle. For the efficient conversion of fluid kinetic energy into work by the blades of the single turbine wheel, the velocity of the supersonic vapor stream exiting from the nozzle mouth (the "spouting" velocity) must bear a definite relation to the blade tip speed. Blade tip speed, in turn, is limited by the strengths of the materials used in wheel fabrication.

Starting with the assumption that automotive turbine wheels must be mass produced using inexpensive, plentiful metals, Sundstrand Aviation Company engineers have determined that a nozzle enthalpy drop of more than 200 Btu per pound of working fluid is excessive. The argument follows.

The metals of low-cost wheel fabrication would likely have yield strengths no greater than 155,000 psi. Sundstrand wheel design practice is to limit the design tensile stress for such a material to 45,000 psi. This corresponds to a wheel tip speed of slightly over 1200 feet per second in a wheel of any diameter having a uniform stress shape, i.e. thick at the hub and thinning with increasing radius. This tip speed, when combined with the design generalizations of Balje (ref. 37) gives, finally, the 200 Btu per pound enthalpy fall limit of this criterion. This is understood to be the isentropic enthalpy fall to the engine exhaust pressure..

6.1.2.7 Criterion 9. Isentropic Expansion Density Ratio $\leqq 25$ (Reciprocating Engine Only - Equivalent Real Cycle) -

The only reciprocating expander considered economically feasible in automobiles is the single stage type. In this type the working fluid is expanded within a cylinder in one step from inlet cutoff volume to blowdown. If the pressure of the fluid falls too little, then too little of the available work of the fluid will be picked up by the piston, and the engine efficiency will be too low.

The obvious way around this limitation is to increase the expansion ratio provided by the cylinder-valving design. But there are mechanical limitations which prevent practical attainment of a cylinder expansion ratio much greater than 25. The limiting factor is the need to provide a minimum cylinder clearance distance and volume to permit unobstructed movement of the inlet valve. Going to a small bore - long stroke design offers no great relief because piston accelerations increase, along with problems associated with bearing lubrication and wear.

Because the working fluid expands on flowing through valves and ports as well as when trapped within the cylinder, and since the former is a totally irreversible change, the criterion is based upon a hypothetical two-step expansion as follows:

Step 1 - fluid expands isentropically from engine inlet condition to an enthalpy equal to the expander exhaust enthalpy

Step 2 - fluid then expands further at constant enthalpy until it reaches the expander exhaust pressure

The cylinder expansion requirement is then simply the density ratio occurring in the first step. The process corresponds to a fully reversible cylinder expansion followed by a fully irreversible blowdown of the vapor to the exhaust.

6.1.3 Cost Criteria

The contractual restriction on fluid cost (Appendix A) is to the effect that the owner's cost for working fluid over the first five years should not exceed $100. This amount includes all direct and indirect costs directly traceable to the working fluid except (by later clarification by EPA) the cost of labor only for any system refills required. Costs are to be based upon a production rate of one million automobiles per year.

Basic to a determination of economic feasibility is the allowable bulk selling price of the fluid FOB the chemical plant at the expected production volume. This can be estimated working backward from the $100 owner cost by subtracting all shipping, packaging, labor, overhead and profit costs accrued between plant sale and customer receipt. Inquiries of several transport companies and internal sources, coupled with operating experience, led to the assignment of expected cost elements as listed in Table 41.

Table 41. MARKUPS AFTER PLANT SALE

		Markup	
Agency	Service	%	$
Original Fill			
Auto Builder	Ship, store, install, profit	60	--
Auto Seller	Transport, check, profit	25	--
Refill			
Distributor	Freight & packaging, per refill (3 gal)	--	0.60
	Warehouse, profit	25	--
Service Station	Stock, profit	35	--

Using these data, the cost distributions of Table 42 were calculated for cases spanning 0 to 3 refills in five years.

Table 42. DISTRIBUTION OF COST

	Distribution of Owner's Working Fluid Cost, Dollars in First 5 Years			
	Number of Refills			
	0	1	2	3
Bulk price, FOB chemical plant	50.0	53.7	54.7	54.9
Auto manufacturer's markup (60%)	30.0	16.1	10.9	8.2
Auto dealer's markup (25%)	20.0	10.7	7.3	5.5
Packaging cost (60¢/refill)	--	0.6	1.2	1.8
Distributor's markup (25%)	--	6.9	9.4	10.7
Service station markup* (35%)	--	12.0	16.5	18.8
Total: auto owner's cost*	100.	100.	100.	100.

---

*Not including installation labor of refills

Under the assumptions, the fluid manufacturer must be able to sell the total 5-year supply of fluid for \$50 to \$55. Translated into price per single charge, and price per gallon assuming a 3-gallon charge, the numbers are:

	Maximum Bulk Sales Price	
Number of Refills	\$/Charge	\$/gal (3-gal Charge)
0	50.0	16.7
1	26.9	9.0
2	18.2	6.1
3	13.7	4.6

These and other cost calculations are conveniently embodied in the formula:

$$C = PW(2 + 1.69N) + 1.01N \qquad (21)$$

where C = owner's fluid cost/5 years
P = bulk price per pound
W = pounds fluid per charge
N = number of refills/5 years

The amount of working fluid to be installed in an average automobile has not been fixed with great certainty. By inquiry of Rankine system contractors in early 1972 it was learned the expectation was for about 40 pounds per vehicle. As this corresponds closely to 3 gallons of high density (1.6 x water) fluid, the 3-gallon charge was assumed from this point on. At an annual production rate of one million automobiles, total fluid demand would be about 40 million pounds per year. Allowing 25% for refills, the expected annual working fluid demand becomes 50 million pounds per year.

Under the set of assumptions made thus far, the highest tolerable bulk fluid price is $1.25 per pound for a fluid of density 13.33 pounds per gallon or $2.00 per pound for a fluid of 8.33 pounds per gallon. To sell at these prices, the fluid would have to function without replacement for five years.

At the outset of this study it was intended to set go/no-go price criteria for candidate screening. Limits were to be set for each of the principal price sources:

1. published bulk prices
2. privately quoted or estimated bulk prices
3. quick-rough estimated bulk prices
4. actual prices of research samples

Early experience with this approach was so poor as to lead to the abandonment of the idea of screening early candidates using cost criteria.

6.1.4 Hazard Criteria

Hazard evaluation is without doubt the most difficult aspect of working fluid selection. Among the reasons for this are the paucity of widely accepted standards, guidelines, protocols, test methods, definitions and the like. Another reason is the economic impracticality of carrying out more than a handful of the simplest of animal toxic exposure experiments, employing only a very few of the most promising materials. While it is recognized that more exhaustive evaluations must be conducted before an organic fluid can be fully recommended for widespread use in Rankine powered vehicles, it was deemed economically impractical to do so before the Rankine engine truly is a viable alternate to the internal combustion engine. In addition, at this writing no detailed environmental and health hazard criteria have been established for rating the acceptability of fluids for the application of this study.

Largely as a consequence, consideration of hazards tends to be highly subjective, from laying down requirements to recommending courses of action. Thus it is a relatively simple matter to declare that the "working fluid and its derivatives will present a negligible health hazard in any physical state when exposed to any ambient or system conditions", but it is quite a different matter to prove that any particular fluid, including water, meets this ambitious requirement. What is, for example, a negligible health hazard? Is a working fluid hazardous simply because it will kill a mouse when fed via stomach tube in the amount of 1 g/kg body weight? Is the detection of phosgene in the products of a fuel-air-working fluid fire sufficient grounds for rejecting the fluid? How can one predict the effect of releasing millions of pounds of working fluid into the environment over a period of years?

Because unequivocal answers to such questions are not to be had, quantitative hazards criteria were not adopted. Instead, a series of hazard-related tests were selected and performed on only the more advanced candidate fluids. The test results were presented in sections 5.6 and 5.7. This does not mean that potential hazards were ignored in screening early fluid candidates. Every reasonable effort was made to exclude from consideration materials known or suspected to be fire-hazardous or toxicity-hazardous.

6.1.5 Compatibility, Stability, Lubrication Criteria

The requirement that the working fluid be compatible with common materials of powerplant construction was partly satisfied in screening Criterion 4, where demonstration of compatibility with carbon steel at 720°F for at least 200 hours is demanded. With this exception, compatibility, stability and lubrication were explored in depth only with respect to the final fluid candidates, as discussed in sections 5.5 and 5.8. Quantitative search criteria were, therefore, not set for these requirements, just as in the case of the hazard requirements.

In choosing candidate fluids, however, these requirements were very much in mind. Very many materials, including nearly all inorganic chemicals having reasonable liquid ranges, were rejected from the search as being incompatible with steel at the 720°F temperature. In searching for compatible lubricants, petroleum oils were shown in special testing (section 6.11) to be unstable at temperatures above 660°F, so only synthetic and non-petroleum oils were seriously considered as working fluid compatible lubricants.

6.2 INITIAL CANDIDATE SELECTION (CRITERIA 1-3)

While it is apparent from contractual requirements that a successful candidate must meet many exacting demands, choice of initial candidates was based on the first four selection criteria. First of all, it was necessary that the prospective fluid be available from some source in quantities sufficient for preliminary testing, as no synthesis effort was contemplated in the contract. Beyond this, the initial selection was based primarily on the normal boiling point of the prospective candidates, coupled with their estimated thermal stability. Melting or flow points were also taken into account, but this property was given wide latitude in Criterion 2 and was not so restrictive.

6.2.1 Normal Boiling Points

As will be seen, some candidates chosen for initial screening boiled somewhat higher than the 250°F (120°C) upper limit of Criterion 3. These were included for various reasons, such as ready availability, or because of a need to experimentally develop thermal stability information.

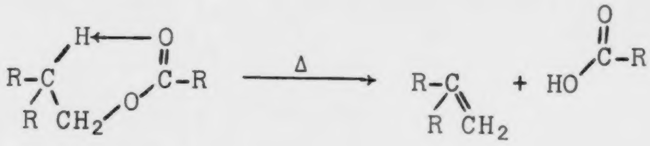
6.2.2 Chemical Structure and Thermal Stability

The ability of organic materials to withstand high temperature depends first of all on the chemical structure of the substrate material. In practice, however, secondary factors, such as the presence or absence of impurities, the types of metals and nonmetals present, sometimes strongly affect the ability of the organic fluid to withstand the thermal stress. In this regard it is useful to consider the term thermochemical stability, which is not synonymous with thermal stability. The latter may be regarded as a property possessed by, in the present context, a Rankine fluid. It is largely independent of the system in which the property is measured. Thermochemical stability, on the other hand, is used to denote the stability of a fluid in its operating environment, i.e., in the presence of metals, lubricants, contaminants, etc. The distinction is important in a practical sense. Thermal stability can be estimated, calculated, or measured with a reasonable degree of efficiency, whereas thermochemical stability generally requires experimental determination under conditions germane to the actual operating system. It is useful in this connection to define the terms decomposition temperature (T_D) and working temperature (T_W). T_D is the temperature at which a certain arbitrarily selected rate of decomposition ensues when a fluid is heated in an "inert" environment. T_W is the maximum temperature at which the fluid has a useful working life. The former almost invariably exceeds the latter by approximately 100-400°F. The T_D-T_W difference depends on such factors as operational conditions, chemical structure of the fluid(s) involved, and the required useful life. Because a great deal more information is available in the literature on thermal stability, initial candidate selection was based on T_D values.

Numerous methods have been employed in the past to measure thermal stability of fluid products. That most widely used today involves some adaptation of the isoteniscope vapor pressure method of A. Smith and A. W. C. Menzies (ref. 38). To measure thermal decomposition temperatures, advantage is taken of the fact that the most general change in properties attending thermal decomposition of organic molecules is an increase in pressure in a containing system. A close relation between isothermal rates of pressure rise and decomposition rates can be readily shown. A plot of log dP/dt vs 1/T is usually a straight line indicating that dP/dt follows an Arrhenius rate law. Hammann (ref. 39) has defined the T_D as the temperature at which dP/dt = 0.014 mm Hg/sec. Details of the apparatus and experimental procedures for measuring T_D are summarized by Hammann (ref. 39), by Blake and co-workers (ref. 40), and by Johns, et al. (ref. 41).

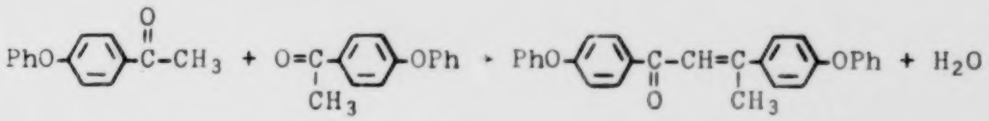
Modern definitive works relating thermal stability and structure of organic compounds stem largely from research on thermally stable lubricants and hydraulic fluids carried out in MRC and Monsanto Company laboratories. Among the best known of these are the extensive studies of Blake and associates (ref. 42-50), beginning in 1955 and continuing to the present. In addition, some particularly useful correlations are given by Johns and co-workers (ref. 41,51) and Sheehan, et al. (ref. 52). Within this large body of data, and in extensive unpublished internal sources, thermal decomposition points (T_D) of several hundred organic compounds are to be found. Many diverse structural types are represented. From these data certain rules of thumb can be formulated which permit estimation of T_D's with reasonable accuracy. In the estimation process, account must be taken of possible mechanistic pathways by which decomposition takes place.

The finite strength of chemical bonds limits the vibrational energy which molecules may possess. Most compounds have pathways of rearrangement at temperatures far below that necessary for straightforward bond rupture. Thus, compounds having configurations or electronic features particularly favoring a low energy pathway will exhibit abnormally low T_D points. An important example illustrates this. Ordinary esters having one or more hydrogens in the β-position of the alcohol moiety show T_D points between 500 and 550°F. Those having the β-position blocked decompose from 40-80°F higher because the low energy decomposition mechanism shown for the unblocked ester is precluded. Many other types of organic materials have comparable low energy pathways by which they may come apart, rearrange, or self-condense. An example of the latter effect is shown by the stability of 4-benzoyldiphenyl ether (T_D = 745°F) as compared to 4-acetyldiphenyl ether (T_D = 351°F) (ref. 40). In the latter case self-condensation occurs



β-hydrogen ester olefin acid

readily with loss of water whereas no such easy reaction is possible in the first instance.



Internal stresses within molecules promote instability. Thus, cyclic carbon compounds and most heterocycles with 3- or 4-membered rings or those with large, 7- to 9-membered rings are appreciably less stable than their unstrained 5- and 6-membered cogeners. Perfluorocyclobutanes and some 4-membered silazanes are exceptions to these generalizations.

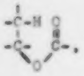
A crude but useful comparison can be made between thermal decomposition of a covalent compound and the breaking of a chain. The strength of the latter depends on its weakest link; thermal decomposition temperature is a function of the weakest bond or combination of bonds. Following this notion one may compile a table of "weak link" bonds along with the approximate temperature at which bond breaking (i.e., decomposition) has been observed to occur. Such a compilation is given in Table 43. With information of this type and some knowledge of decomposition mechanisms, a reasonably accurate assessment of T_D can be made merely by inspection. Inasmuch as a maximum working temperature (T_W) of at least 712°F is required by Criterion 4 in the automotive Rankine application, it was anticipated that only materials having T_D's over ~800°F would have sufficient stability. Ultimately this proved to be the case, but to avoid overlooking any possibilities and as a means of gaining experimental information, many compounds were included in the initial screening list which were judged to have little chance of survival. Almost without exception these initial estimates were confirmed.

6.2.3 Candidate Fluids

Based on normal boiling points, estimations of thermal stability and other considerations, approximately one-hundred pure fluids were collected. These are listed in the following Table 44 along with their normal boiling points and the sample source. For indexing purposes each fluid was assigned a fluid serial number (FSN). From the original list of pure fluids a number of mixtures were then selected for additional examination. Water was an important ingredient in several of the candidate mixtures as indicated in Table 45.

In practice, each fluid sample was checked to see that its boiling point corresponded to that reported in the literature. The sample was also checked for purity by gas liquid chromatography (GLC). If significant impurities were present, the sample was

Table 43. APPROXIMATE THERMAL DECOMPOSITION TEMPERATURES OF ORGANIC COMPOUNDS AS A FUNCTION OF WEAKEST BONDING UNIT

Functionality or Partial Bond Structure Representing Weakest Link in Molecule	Approximate T_D (°F) of Molecule Will Be
$-\overset{\vert}{C}H\overset{O}{\overset{\Vert}{C}}-\overset{\vert}{\underset{\vert}{C}}-$ $-\overset{S}{\overset{\Vert}{C}}R$ $-\underset{\vert}{C}H\overset{NH}{\overset{\Vert}{C}}R$	Low stability functions usually have T_D <350
$-\overset{\vert}{C}HCN$ $-\overset{O}{\overset{\Vert}{C}}-NH_2$ $-\overset{O}{\overset{\Vert}{C}}-ON$, SCN, NC=O	
$-\overset{\vert}{C}HNO_2$ $-NO_2$ $-CHN_2$	
$-\overset{\vert}{C}HSO_2R$ $-\overset{\vert}{C}H\overset{O}{\overset{\vert}{S}}R$ RSH, RSR, RSSR	
$>CH-\overset{\vert}{\underset{\vert}{C}}-$halogen	
$-\underset{\vert}{C}HOH$ R_3COH $R_3COO\overset{O}{\overset{\Vert}{C}}R'$, R_3COR', etc.	
$RO\overset{\vert}{\underset{\vert}{P}}:$ $R_2N\overset{\vert}{\underset{\vert}{P}}:$ (Trivalent Phosphorus) and all $\overset{\vert}{\underset{\vert}{P}}-H$ and $>\overset{O}{\overset{\Vert}{P}}-H$ structures	
$R_3CO\overset{\vert}{\underset{\vert}{P}}=O$ Phosphates of tert alcohols	
and other 3-membered heterocycles	
$>CH\overset{\vert}{\underset{\vert}{C}}-O-\overset{S}{\overset{\Vert}{C}}-$	
$RO\overset{\vert}{\underset{\vert}{P}}=O$, $-C=CCH_2-$	350 - 425
, $>CHOCH<$, $-CH_2OCH<$, $-\overset{O}{\overset{\Vert}{C}}-NR_2$	500 - 550
$R_3CCH_2O\overset{O}{\overset{\Vert}{C}}-$	580 - 615
R_2N-, $R_2N-\overset{\vert}{\underset{\vert}{P}}=O$, $R-\overset{\vert}{\underset{\vert}{P}}:$ $R\overset{\vert}{\underset{\vert}{P}}=O$	550 - 620
$-\overset{\vert}{\underset{\vert}{C}}-\overset{\vert}{\underset{\vert}{C}}-$ $-\overset{\vert}{\underset{\vert}{C}}-H$ aliphatic hydrocarbons only	
(a) cyclic, with internal strain	200 - 580
(b) acyclic, with internal strain	580 - 615
(c) acyclic, without internal strain	630 - 680
$R-\overset{\vert}{\underset{\vert}{Si}}-$, $RO\overset{\vert}{\underset{\vert}{Si}}-$, $RO\overset{\vert}{B}-$	580 - 680
*$ArCH_3$, Ar_2CH_2, $ArCH_2CH_3$, $Ar-\overset{\vert}{\underset{\vert}{Sn}}-$, $Ar\overset{\vert}{\underset{\vert}{Ge}}-$	700 - 730
ArR where $R \geq C_3$, $Ar-\overset{\vert}{\underset{\vert}{P}}:$, $Ar\overset{\vert}{\underset{\vert}{P}}=O$	650 - 700
Ar-Cl, Ar-Br, $ArCF_3$, $ArO-\overset{\vert}{\underset{\vert}{P}}=O$, Ar-S, $Ar-SO_2-$, $Ar\overset{O}{\overset{\Vert}{C}}-$, $(-\overset{\vert}{\underset{\vert}{Si}})_2O$, $ArO\overset{O}{\overset{\Vert}{C}}-$	700 - 800
ArF, $Ar-\overset{\vert}{\underset{\vert}{Si}}-$, $ArO\overset{\vert}{\underset{\vert}{Si}}-$, $ArO\overset{\vert}{B}-$	800 - 850
$Ar(F)_n$ polyfluoro but not perfluoro	750 - 800
Perfluoro aliphatics R_f-O-, R_fS-, $R_fN<$	750 - 850
$Ar-\overset{\vert}{N}-$, Ar-O-, Ar-H, Ar-Ar	850 - 900
Benzene, C_6F_6, certain simple aromatic heterocyclics and many perfluorocarbons (R_f)	>850

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* Ar = Phenyl, biphenyl and certain other relatively simple aromatic systems

Table 44. PURE FLUIDS SELECTED FOR THERMOCHEMICAL STABILITY SCREENING

FSN	Compound	Boiling Pt @ Atm. Press.(°C)	Melting Pt.(°C)	Sample Source*
1	benzotrifluoride	102	-29	Pierce
3	m-bromobenzotrifluoride	154	<-78	Pierce
4	p-bromobenzotrifluoride	154	-4	PCR
6	o-bromofluorobenzene	156	-40	Pierce
7	m-bromofluorobenzene	150	<-18	Pierce
8	bromopentafluorobenzene	137	-31	Pierce
9	p-bromofluorobenzene	151	-17	Pierce
10	p-bromophenyl trifluoromethyl ether	155	-34	Pierce
11	o-chlorobenzotrifluoride	152	-6	Pierce
12	p-chlorobenzotrifluoride	139	-33	Pierce
13	m-chlorobenzotrifluoride	137	-57	Pierce
14	o-chlorofluorobenzene	138	-42	Pierce
15	m-chlorofluorobenzene	126	<-78	Pierce
16	p-chlorofluorobenzene	130	-22	Pierce
17	chloropentafluorobenzene	117	-15	Pierce
18	1,2-dichlorohexafluorocyclobutane	60	-16	PCR
21	1,2-dichlorotetrafluorocyclobutene-1	67	-45	Pierce
22	o-difluorobenzene	92	-34	Pierce
23	p-difluorobenzene	88	-24	Pierce
24	m-difluorobenzene	83	<-78	Pierce
25	2,4-difluorotoluene	115	-49	PCR
26	2,5-difluorotoluene	117	-35	PCR
27	2,6-dimethylfluorobenzene	140	<-78	Pierce
28	2,3-dimethylfluorobenzene	146	-27	PCR
30	1,3-di(trifluoromethyl)benzene	116	-33	Pierce
31	1,4-di(trifluoromethyl)benzene	116	3	Pierce
32	o-fluoroanisole	155	-35	Pierce
33	m-fluoroanisole	158	-34	Pierce

Table 44 Continued

FSN	Compound	Boiling Pt. @ Atm. Press.(°C)	Melting Pt.(°C)	Sample Source*
34	p-fluoroanisole	157	-44	Pierce
35	fluorobenzene	85	-42	Pierce
37	m-fluorobenzotrifluoride	100	-81	Pierce
38	o-fluorobenzotrifluoride	114	-46	Pierce
41	p-fluorophenyl trifluoromethyl ether	105	<-78	Pierce
42	2-fluoropyridine	126	<-78	Pierce
43	o-fluorotoluene	114	-78	Pierce
44	p-fluorotoluene	116	-56	Pierce
45	m-fluorotoluene	117	<-78	Pierce
46	hexafluorobenzene	80	5	PCR
47	methylpentafluorobenzene	117	-30	Pierce
48	octafluorotoluene	104	<-78	PCR
49	pentafluorobenzene	85	-48	Pierce
50	pentafluoropropanol-1	81	-49	Pierce
51	perfluoro(methylcyclohexane)	76	-37	Pierce
52	perfluoroalkane-70	70	<-78	Pierce
53	perfluorotributylamine	170	-50	Pierce
55	perfluoro-2-butyltetrahydrofuran	102	-93	PCR
56	perfluoro(dimethylcyclohexanes)	102	-55	PCR
57	phenyltrifluoromethyl ether	106	-50	PCR
58	phenyltrifluoromethyl sulfide	140	-41	PCR
59	1,2,4,5-tetrafluorobenzene	90	4	PCR
60	1,2,3,5-tetrafluorobenzene	83	-48	PCR
62	2,3,5,6-tetrafluorotoluene	125	-35	PCR
63	trifluoroacetophenone	153	-40	PCR
64	1,2,4-trifluorobenzene	90	-32	PCR
65	1,3,5-trifluorobenzene	75	-5	PCR
66	2,2,2-trifluoroethanol	75	-44	PCR
67	tris(trifluoromethyl)-s-triazine	95	-24	PCR

Table 44 Continued

FSN	Compound	Boiling Pt. @ Atm. Press.(°C)	Melting Pt.(°C)	Sample Source*
69	3-chloropyridine	149	<-78	Aldrich
70	3-methylpyridine	144	-17	Aldrich
71	pyrazine	118	52	Aldrich
73	toluene	110	-95	Fisher
74	methanol	65	-98	Fisher
75	1-propanol	97	-127	Fisher
76	benzene	80	5	Fisher
77	monochlorobenzene	132	-45	Fisher
78	pyridine	115	-42	Fisher
79	tetrachloroethylene	122	-30	Fisher
80	trichloroethylene	87	-35	Fisher
82	2,2,3,3-tetrafluoropropanol	110	-13	PCR
84	perfluoroglutaric anhydride	70	-38	PCR
86	2,4,6-trifluoropyrimidine	98	-2	PCR
88	hexamethyldisilazane	125	-62	Pierce
89	perfluoroether (P-ID)	135	-121	Allied
91	acetic acid	118	17	Fisher
92	morpholine	129	-3	Fisher
93	ethanol	78	-114	Fisher
94	neopentanol	113	52	Aldrich
95	ethylene glycol monomethyl ether	124	-85	Aldrich
96	anisole	154	-37	Fisher
98	N-methylmorpholine	114	<-78	Aldrich
99	thiophene	84	-38	Aldrich
100	1,1,1,2,4,4,4-heptafluoro-2,3,3-trichlorobutane	98	4	Pierce
101	perfluoroheptene-1	82	<-78	Pierce
104	N-nonafluorobutyloctafluoromorpholine	~115	-45	PCR
105	2-methylpyridine	129	-66	Fisher
106	4-methylpyridine	143	4	Fisher

Table 44 Continued

FSN	Compound	Boiling Pt. @ Atm. Press.(°C)	Melting Pt.(°C)	Sample Source*
107	pentafluoropyridine	83	-44	PCR
108	2-chlorothiophene	128	-72	Eastman
109	2,6-dimethylpyridine	143	-7	Eastman
110	2-methylpyrazine	135	-25	Pfaultz
111	hexamethyldisiloxane	100	-63	Pierce
112	trimethyl borate	68	-29	Aldrich

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* Sources

Pierce Chemical Company, Rockford, Illinois 61105
PCR, Inc., Gainseville, Florida 32601
Aldrich Chemical Company, Inc., Milwaukee, Wisconsin 53233
Fisher Scientific, Pittsburgh, Pennsylvania 15219
Allied Chemical, Buffalo, New York
Eastman Organic Chemicals, Rochester, New York 14650
Pfaultz & Bauer, Flushing, New York 11351

Table 45. FLUID MIXTURES SUBJECTED TO THERMO-CHEMICAL STABILITY TESTS

Mixed Fluid No. MFSN	Pure Fluid Serial Nos. FSN - FSN	Mixture
3	93 - 90	ethanol-H_2O
11	75 - 90	n-propanol-H_2O
15	78 - 90	pyridine-H_2O
16	78 - 23	pyridine-p-difluorobenzene
18	78 - 59	pyridine-1,2,3,4-tetrafluoro benzene
19	96 - 23	anisole-p-difluorobenzene
20	66 - 99	2,2,2-trifluoroethanol-water
21	70 - 90	3-methylpyridine-H_2O
22	71 - 90	pyrazine-H_2O
23	105 - 90	2-methylpyridine-water
24	106 - 90	4-methylpyridine-water
25	109 - 90	2,6-dimethylpyridine-water
26	110 - 90	2-methylpyrazine-water

fractionally distilled until material of satisfactory purity was attained. In a few cases the identity of hard-to-separate impurities were determined by combined GLC/mass spectroscopy so as to make sure that no low-stability materials were present. Usually such minor impurities proved to be isomers of the compound in question. Their presence in small amounts (1-5%) was sometimes tolerated when it was felt that thermal stability tests would not be compromised.

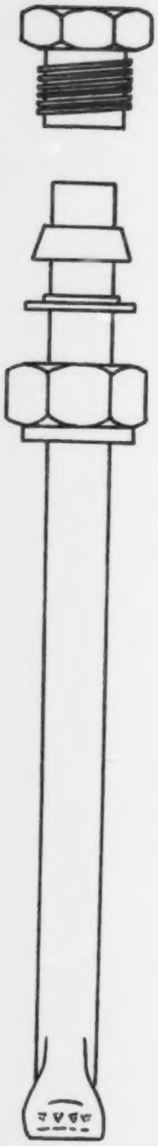
6.3 THERMAL STABILITY SCREENING (CRITERION 4)

All of the pure compounds of Table 44 and the mixtures listed in Table 45 were subjected to a series of ampoule thermostability tests. Details of the ampoule itself and test conditions are outlined in Figure 28.

The SAE 1008 low carbon steel tube used to construct the ampoule was chosen as representing the type of steel ultimately desired for vaporizer fabrication.

In thermostability testing an appropriate number of tubes (up to 50 at a time) were charged with about one milliliter each of fluid. These were then capped with no effort made to exclude ambient air - this to simulate the unsophisticated handling of working fluid which might be anticipated in actual service. After closure, a short wire (about 2 ft in length) was attached to each tube. The tubes were then suspended vertically in an electrically heated fluidized alumina bath. Each alumina bath (two were used in this test work) contained about 2.5 gal of 80-200 mesh alumina. The temperature in each bath could be controlled at any temperature desired up to ~750°F with no more than ±3°F variation. Except for some minor thermostability studies (section 6.11) all test work herein reported was done at 720°F under Criterion 4.

After appropriate exposure times at 720°F, ampoules were removed for examination. The procedure employed was essentially as follows. After cooling to room temperature, each ampoule was inverted (cap down) and cooled to -75°F in an acetone-dry ice bath. While cold, the welded end of each tube was cut off and a rubber septum placed over the open end. A 10 cc disposable syringe was then inserted into the septum and the tube was allowed to come to room temperature. If a condensable gaseous decomposition product was present, its presence was indicated by expansion into the syringe on warming. In this way, too, a gas sample was made available for examination. Liquid contents were then removed and examined in an appropriate manner. Generally this involved qualitative observations of color, solids content and, where appropriate, of acidity. The presence of strong acid was judged to be failing, regardless of other fluid conditions. Other pass-fail criteria were more subjective. Thus, if an exposed sample was clear, though colored, it was judged as having passed. If solids were also present, the sample was usually judged as having failed.



Tube Specifications

SAE 1008 low carbon steel tubing

6 inches long

0.375 in. OD x 0.035 in. wall thickness

Total volume 7.0 ml

Top Fitting - Swagelok S 600-C

Bottom - Crimped and Heliarc Welded

Test Conditions

Vol. test fluid: 0.5 - 2 ml (calc'd to afford max. pressure in 800-1500 psi range)

Test temperature - 720°F.

Test time - variable

Freeboard - room air at atmospheric pressure

Figure 28. Steel Ampoule Thermal Stability Test

In general, where doubt existed, the fluid was either retested or passed to the next time interval - usually 24 hours longer. In this way the thermochemical stability of each candidate fluid was screened. These results are summarized in Table 46.

Concurrent with the thermochemical screening of pure fluids a number of mixed fluids were similarly investigated. These results are summarized in Table 47.

Not surprisingly, nearly one-third of the fluids failed to survive even 24 hours at 720°F. These included all of the simple aliphatic alcohols and, except for trifluoroethanol, all of the partially fluorinated alcohols. Other simple aliphatic acids, amines and ethers decomposed extensively. With the exception of chlorobenzene itself and bromopentafluorobenzene, bromo- and chlorosubstituted aromatics failed. All partially chlorinated or fluorinated alkanes were among the early failures as were perfluoroheptene-1, perfluoroglutaric anhydride, anisole and the monofluoroanisoles. It is noteworthy also that in mixtures with pyridine the fluorinated benzenes decomposed - this despite the fact that separately both components were quite stable at 720°F. Fluids surviving exposures of 24 hours or longer are listed in Table 48.

At this point the question of what constitutes acceptable thermostability must be considered. No agreement exists as to what survival time in a hot ampoule means in terms of real fluid life in a Rankine system. Clearly this is a complicated question. One might conclude that if 10% of the fluid inventory of a Rankine engine were exposed to the elevated temperature (712°F) at any given time, then ampoule life at this temperature might be increased by a factor of ten in a real system. Regardless of the validity of such reasoning, the ampoule test serves to rank fluids in their approximate order of stability in a static mild steel environment. The test serves more to define relative stability of candidates than to forecast their lifetimes in a working system. Far more sophisticated tests are required to do the latter. In the present investigation a survival time of at least 200 hours at 720°F has been considered necessary for a fluid candidate to be of interest. Such fluids are listed in Table 49.

While not entirely evident from the data of Table 46, it became clear during the screening that benzene, toluene, the perfluoro(methylcyclohexanes), P-1D, octafluorotoluene and all of the fluorinated benzenes were stable at 720°F almost indefinitely. Generally the samples survived the two-week exposure without any discernible change. Pyridine, pentafluoropyridine, 1,3-di(trifluoromethyl)benzene and the dimethylfluorobenzenes seemed slightly less stable but survived reasonably well. Pyridine-water, the methylpyridines (and their water mixtures) and some fluorinated toluenes appear to be of lesser stability, with slight decomposition being detectable after 7-10 days. The various classes may thus be grouped approximately as shown in Table 50.

Table 46. RANKINE FLUID CANDIDATES - SUMMARY OF THERMOCHEMICAL SCREENING RESULTS

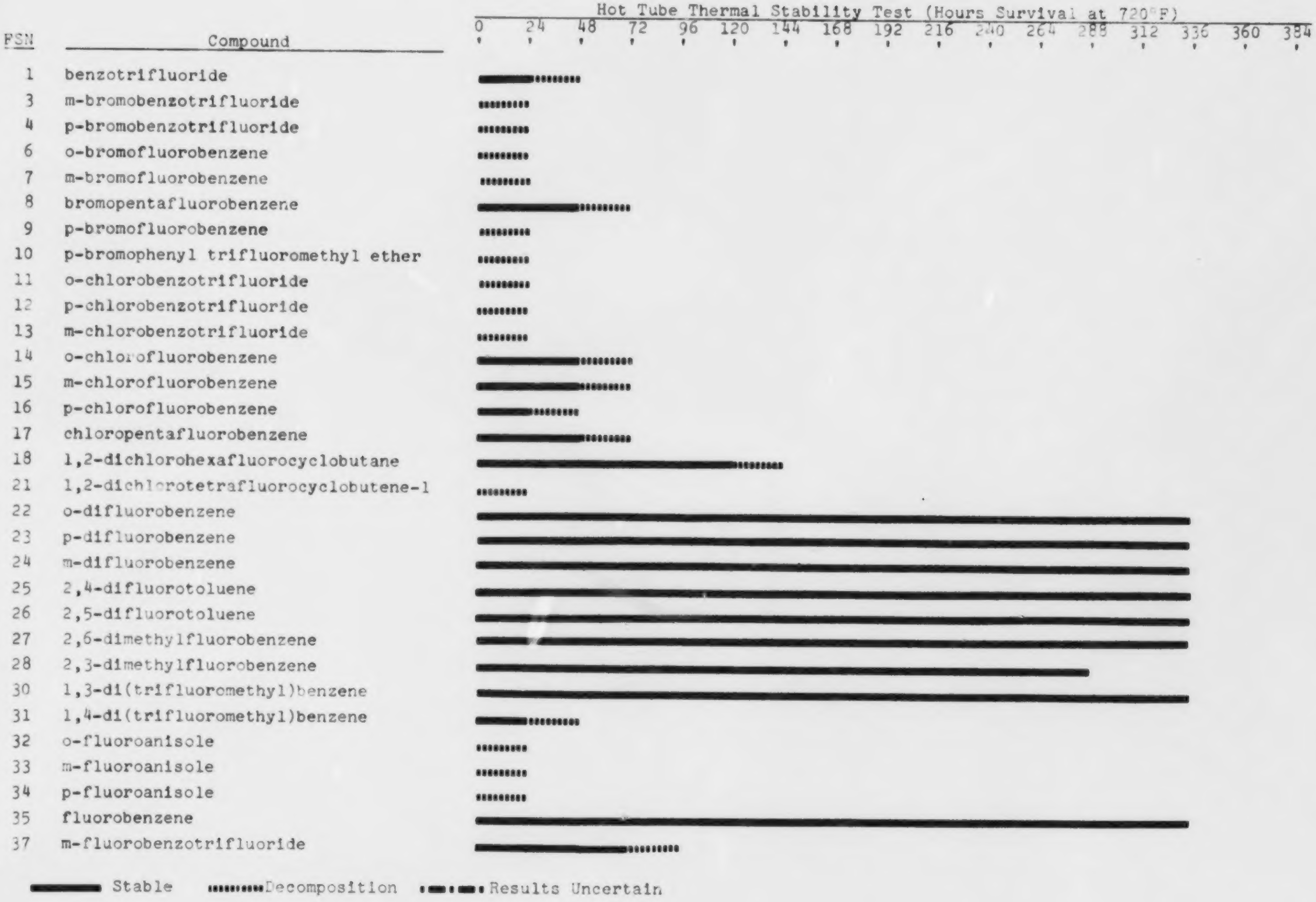


Table 46 Continued

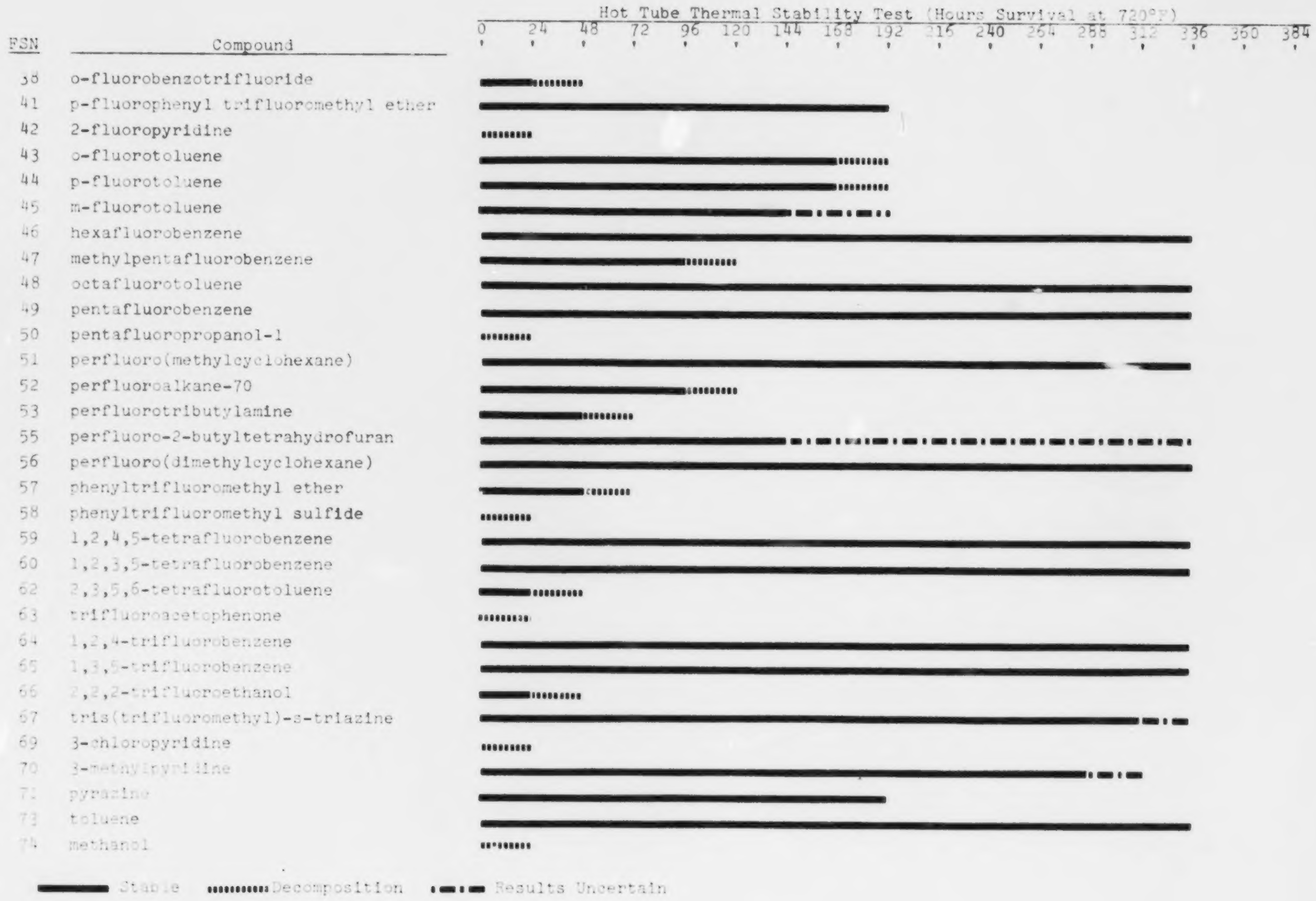


Table 46 Continued

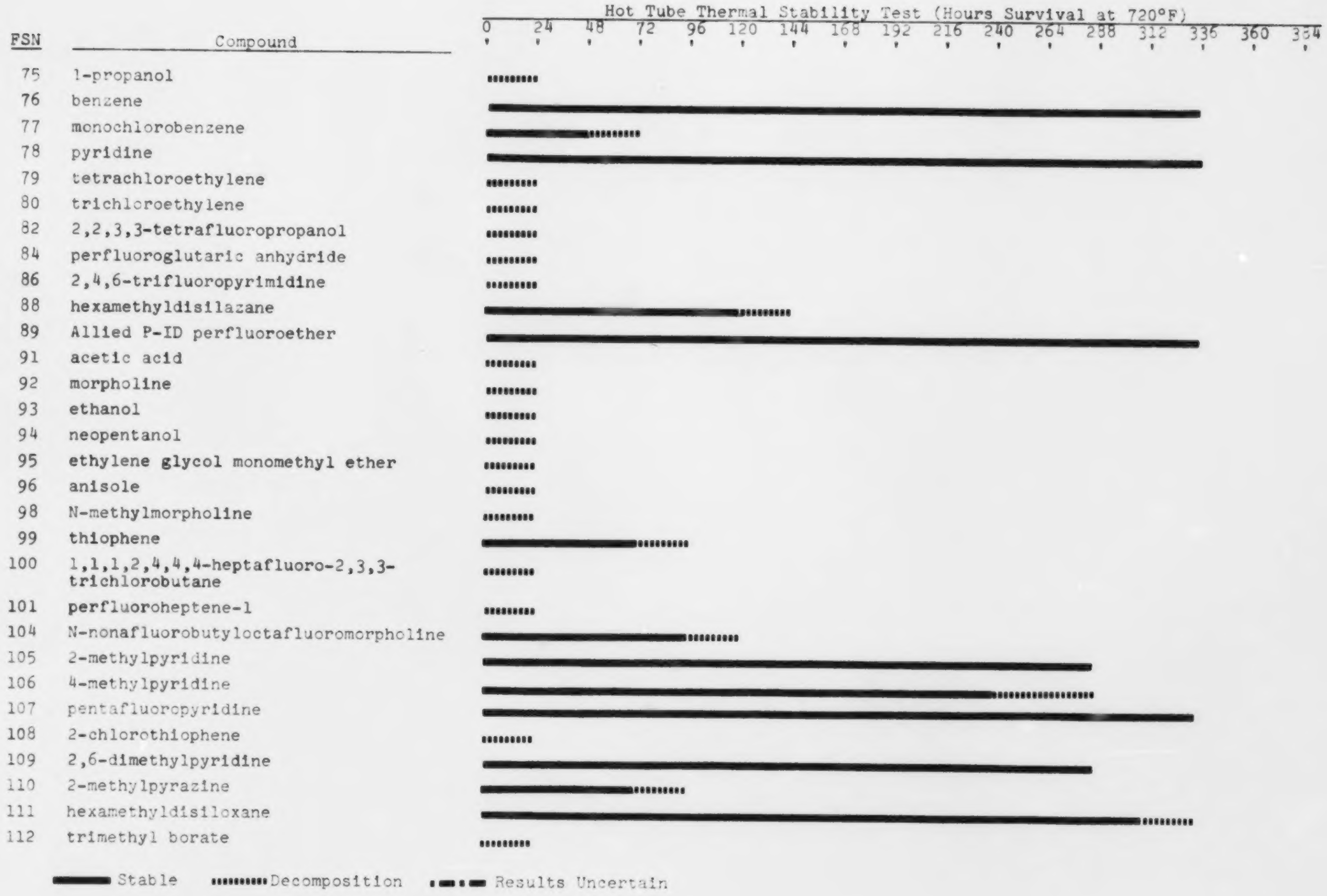
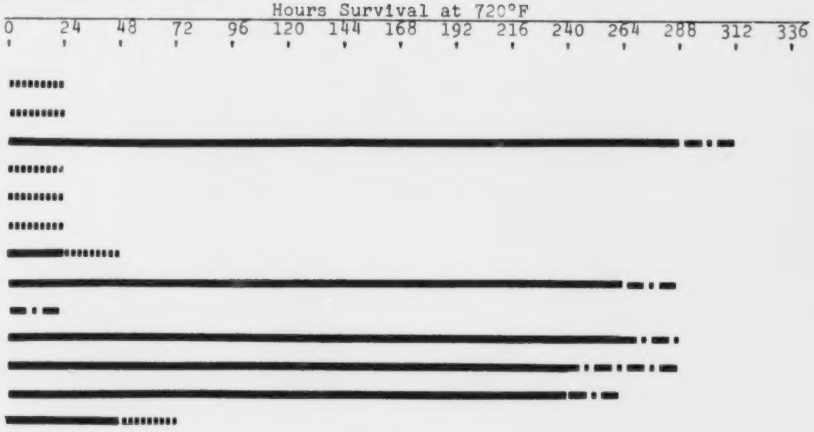


Table 47. STABILITY TESTING OF MIXED FLUIDS

MFSN	Mixture	Mol Fraction Tested
3	ethanol-H_2O	0.5 -0.5
11	n-propanol-H_2O	0.5 -0.5
15	pyridine-H_2O	0.5 -0.5
16	pyridine-p-difluorobenzene	0.5 -0.5
18	pyridine-1,2,3,4-tetrafluorobenzene	0.5 -0.5
19	anisole-p-difluorobenzene	0.5 -0.5
20	2,2,2-trifluoroethanol-H_2O	0.85-0.15
21	3-methylpyridine-H_2O	0.5 -0.5
22	pyrazine-H_2O	0.25-0.75
23	2-methylpyridine-H_2O	0.5 -0.5
24	4-methylpyridine-H_2O	0.5 -0.5
25	2,6-dimethylpyridine-H_2O	0.5 -0.5
26	2-methylpyrazine-H_2O	0.5 -0.5



▬ Stable ┅ Decomposition ━·━ Results Uncertain

Table 48. PURE FLUIDS SURVIVING 720°F STABILITY TEST FOR 24 HOURS OR LONGER

FSN	Fluid	Survival (hr)
1	benzotrifluoride	24
8	bromopentafluorobenzene	48
14	o-chlorofluorobenzene	48
15	m-chlorofluorobenzene	48
16	p-chlorofluorobenzene	24
17	chloropentafluorobenzene	48
18	1,2-dichlorohexafluorocyclobutane	120
22	o-difluorobenzene	>336
23	p-difluorobenzene	>336
24	m-difluorobenzene	>336
25	2,4-difluorotoluene	>240
26	2,5-difluorotoluene	>240
27	2,6-dimethylfluorobenzene	>240
28	2,3-dimethylfluorobenzene	>240
30	1,3-di(trifluoromethyl)benzene	>336
31	1,4-di(trifluoromethyl)benzene	24
35	fluorobenzene	>336
37	m-fluorobenzotrifluoride	72
38	o-fluorobenzotrifluoride	24
41	p-fluorophenyl trifluoromethyl ether	>192
43	o-fluorotoluene	168
44	p-fluorotoluene	168
45	m-fluorotoluene	168
46	hexafluorobenzene	>336
47	methylpentafluorobenzene	96
48	octafluorotoluene	>336
49	pentafluorobenzene	>336
51	perfluoro(methylcyclohexane)	>336

Table 48 Continued

FSN	Fluid	Survival (hr)
52	perfluoroalkane-70	96*
53	perfluorotributylamine	48*
55	perfluoro-2-butyltetrahydrofuran	144*
56	perfluoro(dimethylcyclohexane)	>336
57	phenyltrifluoromethyl ether	48
59	1,2,4,5-tetrafluorobenzene	>336
60	1,2,3,5-tetrafluorobenzene	>336
62	2,3,5,6-tetrafluorotoluene	24
64	1,2,4-trifluorobenzene	>336
65	1,3,5-trifluorobenzene	>336
66	2,2,2-trifluoroethanol	24
67	tris(trifluoromethyl)-s-triazine	~312
70	3-methylpyridine	240
71	pyrazine	192
73	toluene	>336
76	benzene	>336
77	monochlorobenzene	48
78	pyridine	336
88	hexamethyldisilazane	120
89	Allied P-ID perfluoroether	>336
99	thiophene	72
104	N-nonafluorobutyloctafluoromorpholine	96
105	2-methylpyridine	264
106	4-methylpyridine	216
107	pentafluoropyridine	>336
109	2,6-dimethylpyridine	216
110	2-methylpyrazine	72
111	hexamethyldisiloxane	~312

---

* Stability believed to be lowered by the presence of hydrogen-containing impurities.

Table 49. PURE FLUIDS STABLE FOR LONGER THAN 200 HOURS AT 720°F

FSN	Fluid	Survival (hr)
22	o-difluorobenzene	>336
23	p-difluorobenzene	>336
24	m-difluorobenzene	>336
25	2,4-difluorotoluene	>240
26	2,5-difluorotoluene	>240
27	2,6-dimethylfluorobenzene	>240
28	2,3-dimethylfluorobenzene	>240
30	1,3-di(trifluoromethyl)benzene	>336
46	hexafluorobenzene	>336
48	octafluorotoluene	>336
49	pentafluorobenzene	>336
51	perfluoro(methylcyclohexane)	>336
56	perfluoro(dimethylcyclohexane)	>336
59	1,2,4,5-tetrafluorobenzene	>336
60	1,2,3,5-tetrafluorobenzene	>336
64	1,2,4-trifluorobenzene	>336
65	1,3,5-trifluorobenzene	>336
67	tris(trifluoromethyl)-s-triazine	~312
70	3-methylpyridine	~288
73	toluene	>336
76	benzene	>336
78	pyridine	~336
89	Allied P-ID perfluoroether	>336
105	2-methylpyridine	~288
106	4-methylpyridine	~240
107	pentafluoropyridine	>336
109	2,6-dimethylpyridine	~288
111	hexamethyldisiloxane	~312

Table 50. APPROXIMATE ORDER OF STABILITY IN AMPOULE TESTS AT 720°F

Stable Indefinitely	Stable to about 336 hr	Stable for ∿240-312 hr
benzene, toluene	pyridine	pyridine-water
fluorobenzenes	pentafluoropyridine	methylpyridines
octafluorotoluene	1,3-di(trifluoromethyl)benzene	methylpyridine-water
P-ID	methyl-substituted fluorobenzenes	some fluorinated toluenes
perfluorinated-methylcyclohexanes		tris(trifluoromethyl)-s-triazine
		hexamethyldisiloxane

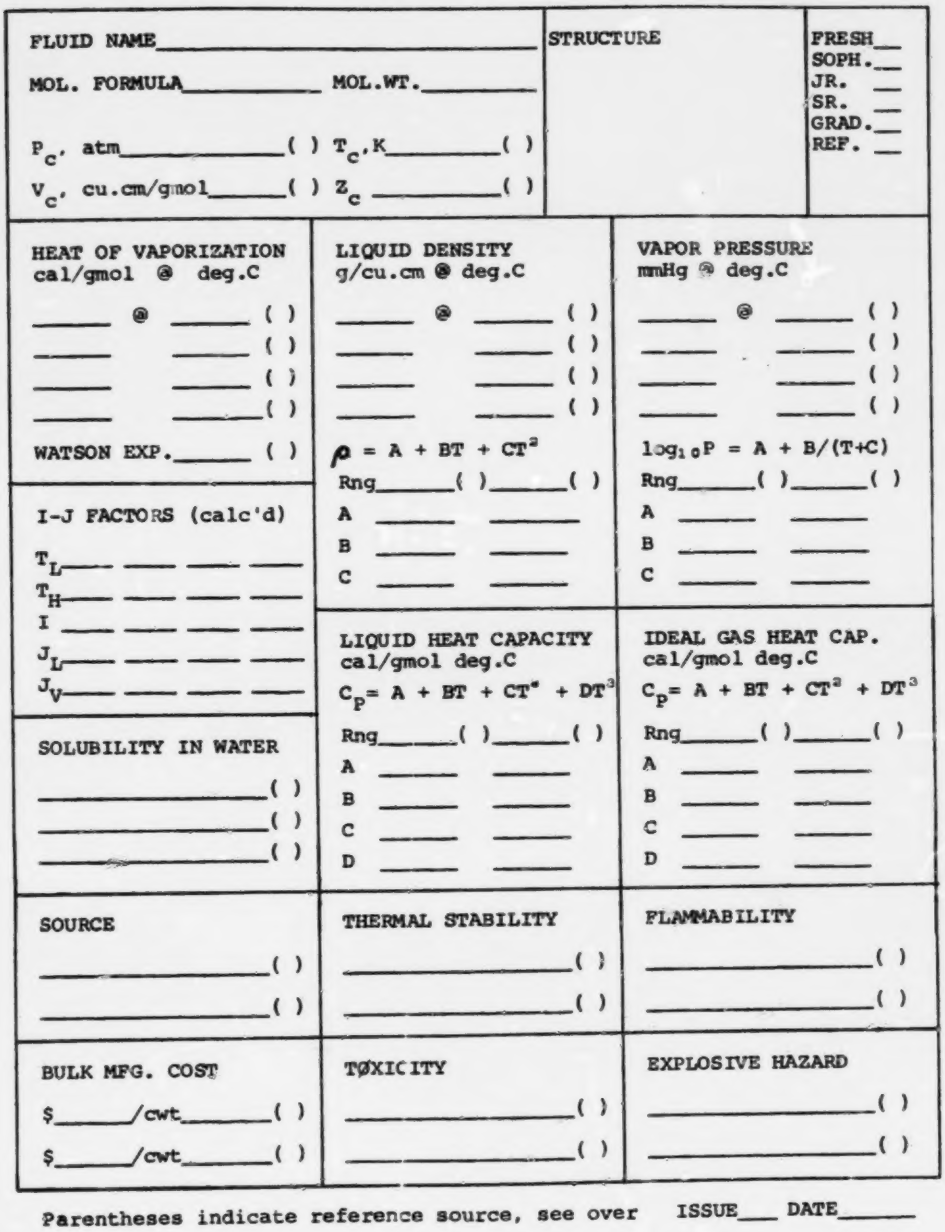
While thermostability testing was in progress other screening criteria were being applied to further refine the selection process. Included in this effort were calculations designed to evaluate the thermodynamic qualities of a candidate fluid or fluid mixture. These approaches will now be outlined.

6.4 PHYSICAL PROPERTIES, LITERATURE AND ESTIMATION

Since the performance of a Rankine cycle engine is significantly dependent on the physical properties of the working fluid, some physical property information had to be retrieved for a large number of compounds. A standard data sheet for recording properties was prepared (see Figure 29 for an example). As physical properties were retrieved from the literature or estimated, they were recorded on these data sheets and the source was recorded on the back. Two large loose-leaf binders were filled with these data sheets and supplementary information. Sheer volume prevents their inclusion in this report, but the notebooks have been filed with EPA as a supplement to this project.

The extent of the literature search was not the same for all compounds. Initially, only those data necessary to compute I-factors (see section 6.5) were retrieved. Properties not readily found were estimated with Monsanto proprietary computer programs. Generally, the estimation methods used were based on those reported in Reid and Sherwood (ref. 53).

As the I-factor and thermal stability tests indicated certain compounds to be more promising as candidates or mixture components of candidates, a more thorough literature search was made, estimated properties were replaced by literature values wherever possible, and sufficient properties were recorded to allow the computation of complete tables of thermodynamic properties (see Appendix K for



FLUID NAME ____

MOL. FORMULA ____ MOL.WT. ____

P_c, atm ____ ( ) T_c,K ____ ( )

V_c, cu.cm/gmol ____ ( ) Z_c ____ ( )

STRUCTURE

FRESH __
SOPH. __
JR. __
SR. __
GRAD. __
REF. __

HEAT OF VAPORIZATION
cal/gmol @ deg.C

____ @ ____ ( )
____ ____ ( )
____ ____ ( )
____ ____ ( )

WATSON EXP. ____ ( )

LIQUID DENSITY
g/cu.cm @ deg.C

____ @ ____ ( )
____ ____ ( )
____ ____ ( )
____ ____ ( )

$\rho = A + BT + CT^2$

Rng ____ ( ) ____ ( )
A ____ ____
B ____ ____
C ____ ____

VAPOR PRESSURE
mmHg @ deg.C

____ @ ____ ( )
____ ____ ( )
____ ____ ( )
____ ____ ( )

$\log_{10}P = A + B/(T+C)$

Rng ____ ( ) ____ ( )
A ____ ____
B ____ ____
C ____ ____

I-J FACTORS (calc'd)

T_L ____ ____ ____ ____
T_H ____ ____ ____ ____
I ____ ____ ____ ____
J_L ____ ____ ____ ____
J_V ____ ____ ____ ____

LIQUID HEAT CAPACITY
cal/gmol deg.C

$C_P = A + BT + CT^2 + DT^3$

Rng ____ ( ) ____ ( )
A ____ ____
B ____ ____
C ____ ____
D ____ ____

IDEAL GAS HEAT CAP.
cal/gmol deg.C

$C_p = A + BT + CT^2 + DT^3$

Rng ____ ( ) ____ ( )
A ____ ____
B ____ ____
C ____ ____
D ____ ____

SOLUBILITY IN WATER

____ ( )
____ ( )
____ ( )

SOURCE

____ ( )
____ ( )

THERMAL STABILITY

____ ( )
____ ( )

FLAMMABILITY

____ ( )
____ ( )

BULK MFG. COST

\$____/cwt____ ( )
\$____/cwt____ ( )

TØXICITY

____ ( )
____ ( )

EXPLOSIVE HAZARD

____ ( )
____ ( )

Parentheses indicate reference source, see over ISSUE___ DATE______

Figure 29. Pure Compound Data Sheet

input data sheets for the thermodynamic grid calculations). The physical properties of the pure components of the advanced candidates are given in section 5.3. Some of the other fluids and mixture components having promising physical properties are recorded in Table 51. Properties of other materials retrieved in this project are recorded in the physical property notebooks.

The computation of thermodynamic properties of liquids requires a knowledge of liquid phase activity coefficients. These quantities have powerful influence on the bubble point and dew point vapor pressures of mixtures. Details of the use of activity coefficients in saturation pressure calculations are given in the description of computer programs developed for this project (see Appendix L). The Van Laar equations have been used throughout this project, and the parameters developed for the more promising fluid pairs are listed in Table 52.

The Van Laar parameters were obtained by processing vapor-liquid equilibrium data through proprietary computer programs of Monsanto Company. Where literature data were not available, vapor pressure curves were measured by isoteniscope for the pure components and two or more mixture compositions. A special computer program (E-1375) was developed to obtain Van Laar constants from the isoteniscope data. This program is described in detail in Appendix L.

6.5 THERMODYNAMIC SCREENING, I-FACTOR (CRITERION 5)

The use of the I-factor (sections 6.1.1.5-7) as a screening tool proved to be extremely useful in the fluid selection process. Under Criterion 5, the range of acceptable values was given as

$$0.65 \lesssim I \lesssim 1.5$$

While thermostability test work was in progress, I-factors were calculated for most of the candidate fluids showing stability longer than 24 hours as shown in Table 53. Elimination of candidates having unacceptable I-factors followed as a logical next step. This is illustrated in Table 54, which shows only those fluids surviving more than 200 hours at 720°F. Candidates are grouped by I-factor with those conforming to the Criterion 5 ranges indicated by parentheses. It is noteworthy that water is the only high I-factor fluid which is stable above 720°F. Of the other stable fluids of Table 54, only pyridine and the methylpyridines are completely miscible with water.

The I-factor criterion limits of 0.65 to 1.5 were arbitrarily chosen at first but were later supported by fairly extensive cycle computations involving both simple and complex (mixture) fluids. This is treated in detail in section 6.10.2.

Table 51. PURE COMPONENT PROPERTIES USED IN THERMODYNAMIC PROPERTY CALCULATIONS

Fluid:	2-Methylpyridine	Water	4-Methylpyridine	3-Methylpyridine	Toluene	Trifluoroethanol
Molecular Wt	93.129	18.016	93.13	93.13	92.142	100
T_c (°K)/T_b	621.1/402.55	647.3/373.15	646/418.54	645/417.29	591.72/383.75	499.83/344
T_c (°F)/T_b	657.98/264.59	705.4/212	702.80/293.37	701/291.12	605.1/230.75	440/159.51
P_c (atm)	45.4	218.2	46	54.02	40.55	48.652
P_c (psia)	667.20	3206.2	676.02	793.88	595.92	714.99
*Z_c	0.297	0.230	0.297	0.2807	0.264	---
*V_c (ft³/lb)	0.05734	0.0503	0.05886	0.0473	0.05495	---
ΔH_{vap} (cal/gmol)	8654	9717	10650	8932	7931	8755.5
at ___°K	402.55	373.15	298.15	417.29	383.75	344
ρ_L (g/cm³)	0.9497	1.000	0.9456	0.94736	0.866	1.3736
at ___°K	288.15	277.15	303.15	303.15	293.15	295.15
**Vapor Pressure						
A	14.402	12.144	9.915	10.810	10.5882	11.8
B	-8986.3	-4203.9	-3595.4	-4214.	-4017.31	-3742.6
C	233.73	-26.75	-55.27	-27.18	-7.762	26.97
***Heat Capacity, Ideal Gas						
A	-4.1626	7.136	22.2633	-4.1626	-8.06559	5.391
B	0.116616	0.00264	-0.0897045	0.116616	0.132327	0.074913
C	-6.68199×10^{-5}	4.59×10^{-8}	4.53193×10^{-4}	-6.68199×10^{-5}	-8.08599×10^{-5}	-5.309×10^{-5}
D	1.301498×10^{-8}	0	-4.10335×10^{-7}	1.3015×10^{-8}	1.8719×10^{-8}	1.3501×10^{-8}

---

*Redlich-Kwong Eq. of State gives $Z_c = 0.333$ for all fluids.

**$\ln P$ (atm) = $A + B/[T\ (°K) + C]$; fit between T_b and T_c.

***C_p (cal/gmol - °K) = $A + BT + CT^2 + DT^3$.

Table 52. VAN LAAR CONSTANTS FOR RANKINE CYCLE MIXTURE CALCULATIONS

Component 1: Component 2:	2-Methylpyridine Water	3-Methylpyridine Water	4-Methylpyridine Water	Trifluoroethanol Water
C_1	3.9654	11.574	68.767	-3.699628
C_2	792.79	-255.43	-14325.	1861.58
C_3	-0.0089793	-0.019551	-0.07005437	0
C_4	11.984	11.704	-1.0535	-2.565628
C_5	-1997.1	-2174.7	602.58	1861.58
C_6	-0.0146616	-0.0134725	2.35243×10^{-4}	0

NOTE: $A_{12} = C_1 + C_2/T + C_3T$; T in °K.
$A_{21} = C_4 + C_5/T + C_6T$.

Table 53. I-FACTORS FOR PURE FLUIDS SURVIVING 720°F STABILITY TEST FOR 24 HOURS OR LONGER

FSN	Fluid	Survival (hr)	I-Factor at NBPt.
1	benzotrifluoride	24	0.56
8	bromopentafluorobenzene	48	0.43
14	o-chlorofluorobenzene	48	0.69
15	m-chlorofluorobenzene	48	0.71
16	p-chlorofluorobenzene	24	0.70
17	chloropentafluorobenzene	48	0.64
18	1,2-dichlorohexafluorocyclobutane	120	0.52
22	o-difluorobenzene	>336	0.78
23	p-difluorobenzene	>336	0.79
24	m-difluorobenzene	>336	0.81
25	2,4-difluorotoluene	>240	0.60
26	2,5-difluorotoluene	>240	0.60
27	2,6-dimethylfluorobenzene	>240	0.50
28	2,3-dimethylfluorobenzene	>240	0.50
30	1,3-di(trifluoromethyl)benzene	>336	0.42
31	1,4-di(trifluoromethyl)benzene	24	0.42
35	fluorobenzene	>336	0.77
37	m-fluorobenzotrifluoride	72	0.55
38	o-fluorobenzotrifluoride	24	0.53
41	p-fluorophenyl trifluoromethyl ether	>192	0.52
43	o-fluorotoluene	168	0.63
44	p-fluorotoluene	168	0.62
45	m-fluorotoluene	168	0.63
46	hexafluorobenzene	>336	0.69
47	methylpentafluorobenzene	96	0.57
48	octafluorotoluene	>336	0.55
49	pentafluorobenzene	>336	0.71
51	perfluoro(methylcyclohexane)	>336	0.40

Table 53 Continued

FSN	Fluid	Survival (hr)	I-Factor at NBPt.
52	perfluoroalkane-70	96*	0.26
53	perfluorotributylamine	48*	0.12
55	perfluoro-2-butyltetrahydrofuran	144*	--
56	perfluoro(dimethylcyclohexane)	>336	0.27
57	phenyltrifluoromethyl ether	48	0.54
59	1,2,4,5-tetrafluorobenzene	>336	0.74
60	1,2,3,5-tetrafluorobenzene	>336	0.75
62	2,3,5,6-tetrafluorotoluene	24	0.59
64	1,2,4-trifluorobenzene	>336	0.77
65	1,3,5-trifluorobenzene	>336	0.77
66	2,2,2-trifluoroethanol	24	--
67	tris(trifluoromethyl)-s-triazine	~312	0.36
70	3-methylpyridine	240	0.82
71	pyrazine	192	0.84
73	toluene	>336	0.67
76	benzene	>336	0.89
77	monochlorobenzene	48	0.74
78	pyridine	336	0.87
88	hexamethyldisilazane	120	0.33
89	Allied P-ID perfluoroether	>336	0.28
99	thiophene	72	1.35
104	N-nonafluorobutyloctafluoromorpholine	96	--
105	2-methylpyridine	264	0.56
106	4-methylpyridine	216	0.82
107	pentafluoropyridine	>336	0.75
109	2,6-dimethylpyridine	216	0.75
110	2-methylpyrazine	72	--
111	hexamethyldisiloxane	~312	0.35

---

* Stability believed to be lowered by the presence of hydrogen-containing impurities.

Table 54. THERMALLY STABLE COMPONENTS AND I-FACTORS

FSN	Name	Hours Stable at 720°F	NBPt I-Factor	Result* Crit.3
56	perfluoro(dimethylcyclohexane)	>336	0.27	0
89	perfluoroether P-ID (Allied)	>336	0.28	X
111	hexamethyldisiloxane	312	0.35	0
67	tris(trifluoromethyl)-s-triazine	>312	0.36	0
51	perfluoro(methylcyclohexane)	>336	0.40	0
30	1,3-di(trifluoromethyl)benzene	>336	0.42	0
28	2,3-dimethylfluorobenzene	>288	0.50	X
27	2,6-dimethylfluorobenzene	>336	0.50	X
48	octafluorotoluene	>336	0.55	0
105	2-methylpyridine	>288	0.56	X
25	2,4-difluorotoluene	>336	0.60	0
26	2,5-difluorotoluene	>336	0.60	0
73	toluene	>336	0.66	0
46	hexafluorobenzene	>336	0.68	0
49	pentafluorobenzene	>336	0.71	0
59	1,2,4,5-tetrafluorobenzene	>336	0.74	0
60	1,2,3,5-tetrafluorobenzene	>336	0.75	0
107	pentafluoropyridine	>336	0.75	0
109	2,6-dimethylpyridine	>288	0.75	X
64	1,2,4-trifluorobenzene	>336	0.76	0
65	1,3,5-trifluorobenzene	>336	0.76	0
35	fluorobenzene	>336	0.77	0
22	o-difluorobenzene	>336	0.78	0
23	p-difluorobenzene	>336	0.79	0
24	m-difluorobenzene	>336	0.81	0
70	3-methylpyridine	288	0.82	X
106	4-methylpyridine	240	0.82	X
78	pyridine	>336	0.87	0
76	benzene	>336	0.89	0
90	water	-	2.81	0

---

* 0 = pass, X = fail

6.6 COST PROJECTIONS AND SCREENING

As described earlier (section 6.1.3), it was originally anticipated that a price for each candidate could be easily found or estimated. Prices were obtained for many of the compounds on the initial candidate list from the Oil, Paint and Drug Reporter, a trade paper of the chemical industry, or from private communications with current suppliers for candidates that were not articles of commerce. The resulting list, with prices and price sources noted, is given in Table 55.

Two things became apparent very quickly. "Articles of commerce", which could be priced quickly from such sources as Oil, Paint and Drug Reporter, were almost as quickly eliminated from the lists by failing to meet other criteria. Second, those less common candidates for which suppliers could be found were usually eliminated on technical grounds before correspondence concerning their price could be completed. It was obvious, then, that technical screening was quicker and more effective than economic screening.

In addition, it became obvious that most common materials, whose prices would likely meet the contract requirement of $100 maximum cost over the life of a vehicle, would not meet the technical criteria. The economic question then became, how much will the fluid cost a vehicle owner (and how can these costs be minimized); not, which of the fluids that meet the $100 limit are the best technological choice.

At this point in the work, economic screening was abandoned and additional work along these lines was confined to predictions of the cost of only the final candidate fluids, as presented earlier in section 5.9.

6.7 FLAMMABILITY TESTING

Contractual requirements relating to fire and explosion hazards stated that the "....working fluid and its derivatives will not be capable of sustaining combustion under atmospheric conditions or in a high temperature environment once the auxiliary source of combustion has been removed. Explosion hazards from working fluid vapor/air mixtures shall be minimized and a test used to demonstrate this."

Tests selected to establish flammabilities of candidate fluids included traditional flash/fire/autoignition temperatures and a specialized "hot compartment ignition test". Not all candidates were subjected to flammability tests. Aside from the two final candidates, whose test results were given earlier in section 5.7, most experimental effort was directed to the various organic/water mixtures proposed as candidates.

Table 55. PUBLISHED AND ESTIMATED PRICES OF SELECTED FLUIDS

Defined Organic Component		Bulk Price, $/lb	
FSN	Name	Published[1]	Estimated[2]
22	o-difluorobenzene		7.20
23	p-difluorobenzene		5.80
24	m-difluorobenzene		10.00
35	fluorobenzene		1.10
46	hexafluorobenzene		12.00
49	pentafluorobenzene		12.00
59	1,2,4,5-tetrafluorobenzene		12.00
60	1,2,3,5-tetrafluorobenzene		12.00
70	3-methylpyridine	0.60	
71	pyrazine		1.00
73	toluene	0.03	
76	benzene	0.03	
78	pyridine	0.52	
81	trichloroethane	0.13	
82	2,2,3,3-tetrafluoropropanol		12.00
105	2-methylpyridine	0.46	
106	4-methylpyridine	0.40	
Defined Mixtures			
MFSN	Components		
1	FSN-73 and FSN-78	0.14	
3	FSN-90 and FSN-93	0.01	
5	FSN-75, FSN-76 and FSN-90	0.03	
6	FSN-76, FSN-90 and FSN-93	0.04	
7	FSN-73 and FSN-75	0.08	
8	FSN-75 and FSN-76	0.05	
9	FSN-73 and FSN-74	0.02	
10	FSN-74 and FSN-76	0.02	
12	FSN-74, FSN-78 and FSN-90	0.18	
13	FSN-73 and FSN-76	0.03	
14	FSN-71 and FSN-90	0.62	
15	FSN-78 and FSN-90	0.42	
17	FSN-30 and FSN-78	1.60	
23	FSN-90 and FSN-105	0.30	
24	FSN-90 and FSN-106	0.25	

---

[1] From Oil, Paint and Drug Reporter, 1972
[2] From private estimates

6.7.1 Flash and Fire Point Results

A modification of the Cleveland Open Cup method of ASTM procedure D92 was employed. In this test, a small sample of the working fluid is heated continuously in a cup. Periodically, a small gas flame is passed over the cup. The flash point is the lowest fluid temperature at which ignition is observed, and the fire point is that temperature where sustained burning occurs. The modifications, described in detail in Appendix N, were made to reduce the amount of sample required and to accommodate the above-normal vapor pressures of the working fluids. Principal results are listed in Table 56. The data show that increased water content increased the flash/fire points of the flammable organics, but in no case at concentrations below 90 mol % did its presence prevent ignition altogether.

6.7.2 Hot Compartment Spray Ignition Results

This test was used to assess ignition and explosion hazards of working fluid candidates. The apparatus consists essentially of a cylindrical chamber with heated walls fitted with a spark igniter, a spray injection assembly, and a loose-fitting lid. Additional details are given in Appendix O. In use, the chamber is brought to a desired temperature (after thoroughly flushing with air), the arc is started, and the test fluid introduced as a fine spray through an atomizing nozzle. The occurrence and intensity of ignition are observed via an accelerometer pickup shock meter reading, while any resulting energy released by combustion is recorded as a compartment temperature increase.

Generally, two types of combustion and variations take place in the hot compartment spray test. When the fluid is introduced at high pressure (e.g. 1000 psig), a fluid-rich atmosphere is created around the spark ignition source. The ensuing rapid ignition consumes the air present and no sustained fire follows. The second condition is under low pressure spray where a lower fuel air ratio exists which favors slow ignition, creating high enough compartment temperatures to induce more air from outside the compartment to sustain a fire until the fluid is totally consumed.

The results of the hot compartment spray ignition tests of several fluids are contained in Table 57.

6.8 PHYSICAL PROPERTY MEASUREMENTS

Literature search and estimation techniques were used to produce physical properties for all simple fluids, as described in section 6.4. When dealing with mixtures, however, predictions are not so reliable, and literature data is often non-existent. Measurements are then required to obtain reliable properties. Measurements of vapor pressures and flow points were taken with several of the more promising mixture candidates.

Table 56. FLASH AND FIRE POINTS OF MIXED FLUIDS

Fluid		Flash Point (°F)	Fire Point (°F)
MFSN-15 pyridine/water			
mol % pyridine =	100	85	90
	75	90	95
	50	95	105
	35	100	110
	25	115	130
	15	125	150
	10	130	160
MFSN-20 trifluoroethanol/water			
mol % trifluoroethanol =	85*	105	160**
MFSN-21 3-methylpyridine/water			
mol % 3-methylpyridine =	100	115	120
	75	125	145
	50	130	160
	15	165	190
MFSN-23 2-methylpyridine/water			
mol % 2-methylpyridine =	100	90	100
	75	90	105
	40	120	145
	15	135	175
MFSN-24 4-methylpyridine/water			
mol % amine =	75	125	155
	50	135	180
	30	150	205
	15	175	210
MFSN-25 2,6-dimethylpyridine/water			
mol % amine =	35	140	200
MFSN-28 pentafluorobenzene/hexafluorobenzene			
mol % penta =	60	None	None

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* Same as "Fluorinol-85"

** Mild, low-intensity, perimeter flame

Table 57. HOT COMPARTMENT IGNITION TEST RESULTS

Test Conditions

Initial fluid reservoir charge = 30 cc
Compartment temperature = 100°C (212°F)
Compartment environment = air
Spray time = 1/4 sec

		Fluid Reservoir		Fire Results			
Test No.	Fluid	Pressure (psig)	Temp. (°C)	Compartment Temp. Rise (°C)	Shock Meter Reading	Flash Ignition	Post Ignition Fire
1,2	FSN-76	1000	540	87	15	Yes	Long
	Benzene	1000	565	60	25	Yes	None
		1000	595	63	12	Yes	None
		1000	620	58	8	Yes	None
		500	500	107	10	Yes	Long
		500	530	75	7	Yes	None
		100	330	143	4	Yes	Long
		70	500	134	5	Yes	Long
13	FSN-76	1000	500	45	8	Yes	None
	Benzene	1000	550	30	15	Yes	None
		1000	580	60	15	Yes	None
		1000	610	58	10	Yes	None
		500	500	74	20	Yes	Long
		500	490	62	5	Yes	None
		100	360	140	2	Yes	Long
		100	380	135	2	Yes	None
5	MFSN-15	1000	520	70	10	Yes	None
	Py:H_2O	1000	540	102	15	Yes	Long
	50 mol %	1000	550	80	10	Yes	None
		1000	560	74	12	Yes	None
		500	470	138	20	Yes	Long
		500	480	142	7	Yes	Long
		100	320	140	1	Yes	Long
		100	320	128	1	Yes	Long
15	MFSN-15	1000	520	64	12	Yes	None
	Py:H_2O	1000	540	100	8	Yes	Long
	50 mol %	1000	550	74	14	Yes	None
		1000	560	62	18	Yes	None
		500	460	80	18	Yes	None
		500	500	118	3	Yes	Long
		100	335	205	1	Yes	Short
		100	410	163	2	Yes	Short
8	MFSN-20	1000	410	98	3	Yes	None
	TFE:H_2O	1000	440	88	10	Delayed	None
	85 mol %	1000	460	47	15	Delayed	None
		1000	970	78	16	Delayed	None
		500	390	85	4	Delayed	None
		500	400	87	3	Delayed	None
		100	270	0	0	No	None
		100	280	160	0	Delayed	Long
		100	285	80	0	Delayed	Long

Table 57 Continued

		Fluid Reservoir		Fire Results			
Test No.	Fluid	Pressure (psig)	Temp. (°C)	Compartment Temp. Rise (°C)	Shock Meter Reading	Flash Ignition	Post Ignition Fire
14	MFSN-20 TFE:H_2O 85 mol %	1000	390	93	1	Delayed	None
		1000	425	53	4	Delayed	None
		1000	450	62	15	Yes	None
		1000	465	62	5	Delayed	None
		500	405	76	13	Delayed	None
		500	400	84	2	Delayed	None
		500	400	88	8	Delayed	None
		100	265	142	1	Yes	Short
		100	270	--	--	No	None
		100	270	96	1	Yes	Short
6	MFSN-21 $3CH_3Py:H_2O$ 50 mol %	1000	560	102	7	Yes	None
		1000	590	67	7	Yes	None
		1000	610	70	7	Yes	None
		1000	620	67	4	Yes	None
		500	530	108	4	Yes	Long
		500	545	127	3	Yes	Long
		100	360	112	1	Yes	None
		100	320	119	2	Yes	None
11	MFSN-21 $3CH_3Py:H_2O$ 50 mol %	1000	560	80	20	Yes	None
		1000	580	52	7	Yes	None
		1000	605	66	4	Yes	None
		1000	630	80	2	Yes	None
		500	550	124	2	Yes	Long
		500	590	119	2	Yes	Long
		100	440	125	2	Yes	None
		100	470	140	1	Yes	None
7	MFSN-23 $2CH_3Py:H_2O$ 35 mol %	1000	520	90	8	Yes	None
		1000	530	64	6	Yes	None
		1000	535	68	8	Yes	None
		1000	535	77	6	Yes	None
		500	450	92	3	Yes	None
		500	460	100	7	Yes	Long
		100	320	180	1	Yes	Short
		100	350	158	2	Yes	Short
9	MFSN-23 $2CH_3Py:H_2O$ 35 mol %	1000	460	74	5	Yes	None
		1000	510	60	8	Yes	None
		1000	530	72	10	Yes	None
		1000	540	72	10	Yes	None
		500	450	88	3	Yes	None
		500	460	132	1	Yes	None
		100	330	159	1	Yes	Long
		100	320	132	2	Yes	Long
		100	310	166	2	Yes	Long

Table 57 Continued

		Fluid Reservoir		Fire Results			
Test No.	Fluid	Pressure (psig)	Temp. (°C)	Compartment Temp. Rise (°C)	Shock Meter Reading	Flash Ignition	Post Ignition Fire
3	MFSN-24 $4CH_3Py:H_2O$ 35 mol %	1000	540	35	13	Yes	None
		1000	550	0	0	No	None
		1000	550	75	15	Yes	None
		1000	550	72	12	Yes	None
		500	480	132	2	Yes	Long
		500	490	93	6	Yes	None
		100	380	155	1	Yes	Short
		60	500	150	1	Yes	Short
12	MFSN-24 $4CH_3Py:H_2O$ 35 mol %	1000	535	67	15	Yes	None
		1000	545	65	8	Yes	None
		1000	560	60	5	Yes	None
		1000	565	65	25	Yes	None
		500	475	79	5	Yes	None
		500	485	88	1	Yes	None
		100	390	122	1	Yes	Short
		100	420	125	1	Yes	Short
4	MFSN-25 2,6-Lutidine:H_2O 35 mol %	1000	550	65	0	No	None
		1000	565	107	10	Yes	None
		1000	570	70	7	Yes	None
		1000	590	80	13	Yes	None
		1000	625	77	7	Yes	Short
		500	540	105	30	Yes	Long
		100	480	116	2	Yes	None
		100	550	108	2	Yes	None
10	MFSN-25 2,6-Lutidine:H_2O 35 mol %	1000	520	--	--	No	None
		1000	550	80	10	Yes	None
		1000	565	84	8	Yes	None
		1000	570	80	20	Yes	None
		500	480	95	4	Yes	None
		500	520	91	4	Yes	None
		100	320	134	2	Yes	Long
		100	320	152	2	Yes	Short
16	MFSN-28 C_6F_5H 60 mol % C_6F_6 40 mol %	1000	500	-18	0	No	None
		1000	545	-19	0	No	None
		500	480	-15	0	No	None
		500	495	-14	1	No	None
		500	550	-11	1	No	None
		100	305	17	1	Slight*	None
		100	380	14	2	Slight	None
		100	500	6	1	Slight	None

---

* During sparking, the pyrolysis products from the fluid caught in the spark do burn but do not sustain burning after spark stops.

6.8.1 Vapor Pressure

Vapor pressures were measured using a Monsanto-developed recording tensimeter described in detail in Appendix P. The pressure of a confined liquid-vapor sample at a particular temperature generally depends upon both the overall sample composition and the fraction of the sample which is in the vapor state. If the sample is all liquid but vaporization is just starting, the pressure is referred to as the bubble point pressure and the fluid is said to be at its bubble point. When the sample is all vapor with condensation just starting, the equivalent condition is the dew point. Between these extremes, which may differ considerably at either fixed pressure or temperature, the pressure is meaningful only when related to the degree of vaporization.

A simple fluid shows no change in pressure during isothermal vaporization. Its dew and bubble points are identical, and its single pressure of vaporization is properly called its vapor pressure. Most complex fluids have dew points several to many degrees higher than bubble points at a fixed pressure. An azeotrope, which is a highly non-ideal complex fluid, is an exception to this, but only at one particular temperature (or pressure) where its dew and bubble points coincide.

"Vapor pressures" measured with the recording tensimeter are the pressures obtained with the sample bulb half filled (by volume) with liquid at the beginning of the measurement. This corresponds closely to the bubble point condition at temperatures and pressures well below critical, where vapor densities are negligibly small compared to liquid densities.

In Table 58 appear vapor pressures measured with the water-ethanol system. This mixture was used as a well-known standard exhibiting non-ideal behavior for the development of the mathematical procedures for calculating mixture thermodynamics. Vapor pressures of the final candidate fluids were given earlier in section 5.2.

6.8.2 Flow Points

When a liquid solution is slowly cooled a temperature is reached where first crystals appear. The only visual evidence may be a cloudiness of the fluid. If cooling is continued, the crystals grow in size and number to the point where the liquid's mobility is noticeably diminished. This point, peculiar to complex fluids, is referred to in this study as the flow point.

A simple fluid or a eutectic solidifies completely at a single temperature normally called the freezing or solidification point. Complex fluids otherwise solidify over a range of temperatures. The flow point then represents the lowest temperature at which the fluid, simple or complex, can be expected to function in an engine.

Table 58. VAPOR PRESSURES IN PSIA - ETHANOL/WATER

Temp (°C)	Mol Fraction Ethanol				
	0.0	0.25	0.50	0.75	1.00
50	1.8	4.3	5.0	5.0	4.3
75	5.6	11.6	13.3	13.9	13.0
100	14.7	28.2	31.3	32.8	32.8
125	33.7	(59)	(66)	(70)	72
150	69	122	132	142	143
175	129	224	246	264	254
200	225	370	410	430	429
225	370	580	660	690	676
250	577	850	950	(1020)	--

NOTE: Figures in brackets are literature data.
Figures in parentheses are extrapolated.

The flow points measured with several of the advanced candidates are presented in Figures 30 to 32.

6.9 THERMODYNAMIC TABLE/DIAGRAM COMPUTATIONS

Two special computer programs were developed to compute thermodynamic tables and diagrams for this project. Program E-1393 prepares thermodynamic property tables. It is described in detail in Appendix K. Program TSPLOT interfaces with E-1393 to produce temperature-entropy diagrams. It is described in detail in Appendix M.

Thermodynamic tables and TS diagrams were prepared for a number of fluids. Tables and charts for the advanced candidates are covered in section 5.3. The other tables and charts are not included in this report because of excessive volume. They have been filed with EPA. A list of fluids for which charts have been filed is given in Table 59.

Table 59. FLUIDS FOR WHICH THERMODYNAMIC TABLES AND CHARTS HAVE BEEN PREPARED

Component 1	Component 2	Mol percents (1/2)
Trifluoroethanol	Water	100/0
Trifluroethanol	Water	85/15
Pentafluorobenzene	Hexafluorobenzene	100/0
Pentafluorobenzene	Hexafluorobenzene	60/40
Pentafluorobenzene	Hexafluorobenzene	0/100
4-Methylpyridine	Water	40/60
4-Methylpyridine	Water	30/70
Toluene	--	100/--
Ethanol	Water	60/40
Pyridine	Water	10/90; 20/80; 30/70; 40/60; 50/50; 75/25; 100/0
2-Methylpyridine	Water	10/90; 20/80; 30/70; 40/60; 50/50; 75/25; 100/0
3-Methylpyridine	Water	10/90; 20/80; 30/70; 40/60; 50/50; 75/25; 100/0

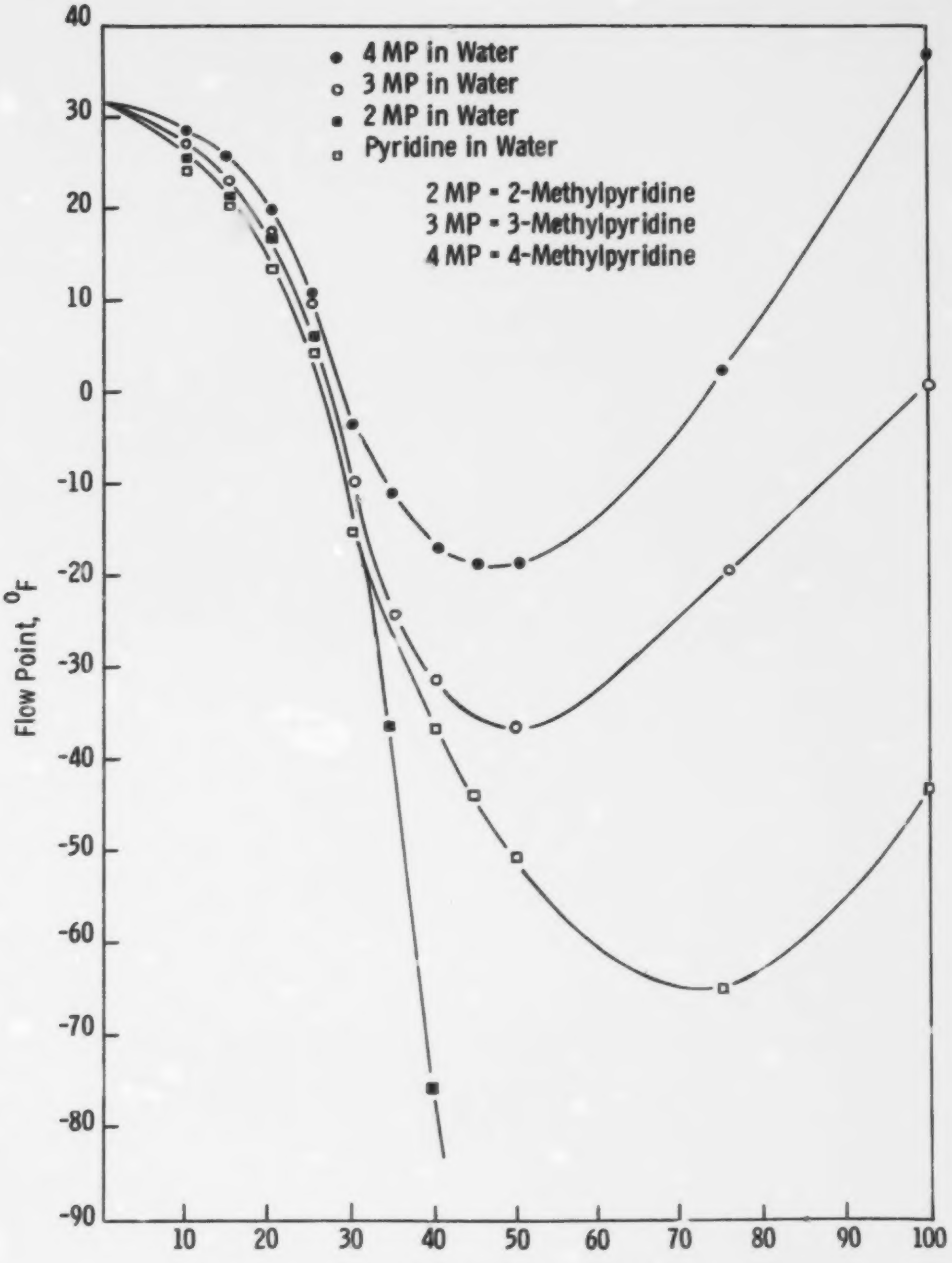

Figure 30. Flow Points - Binary Aqueous Pyridines

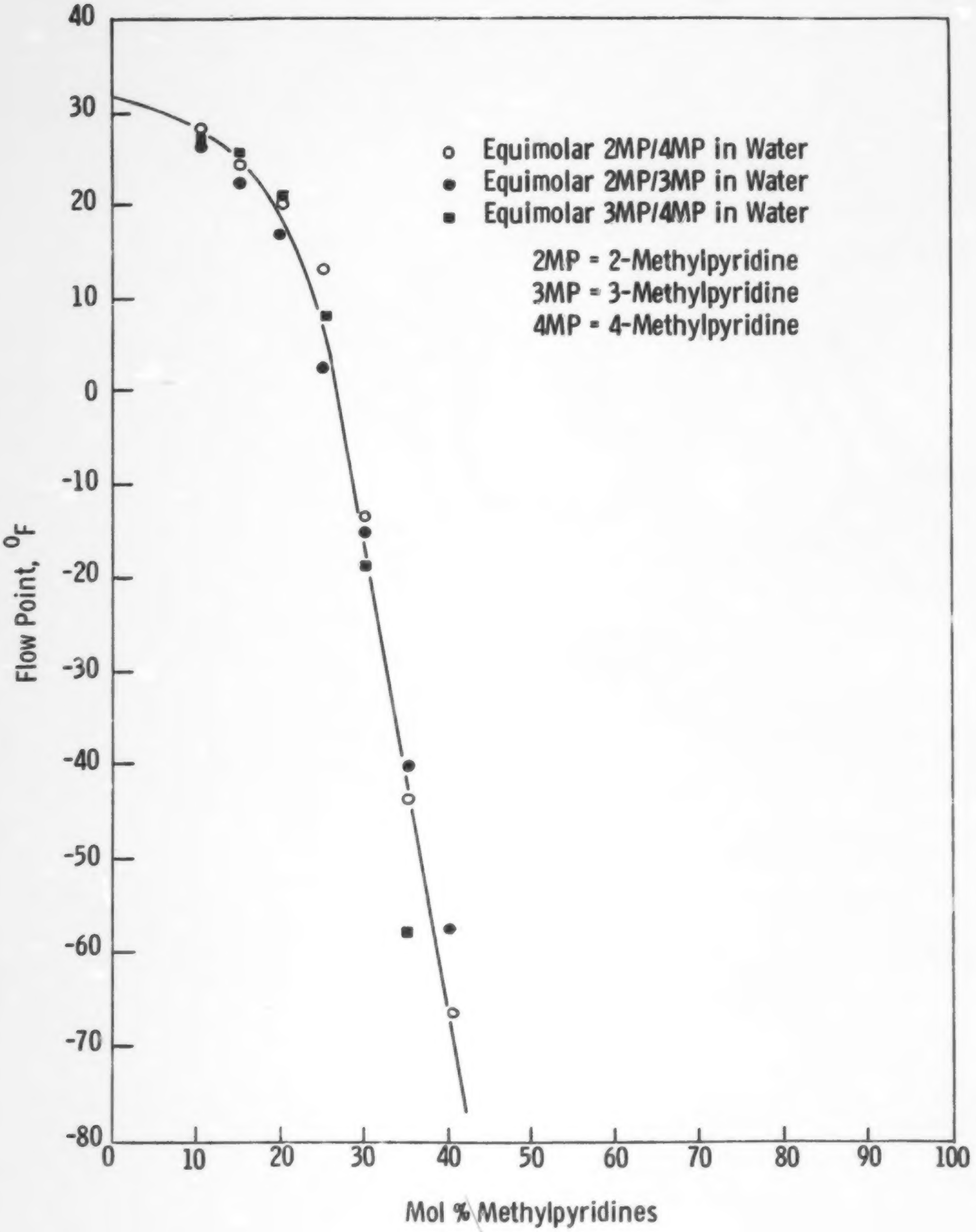

Figure 31. Flow Points - Ternary Aqueous Pyridines

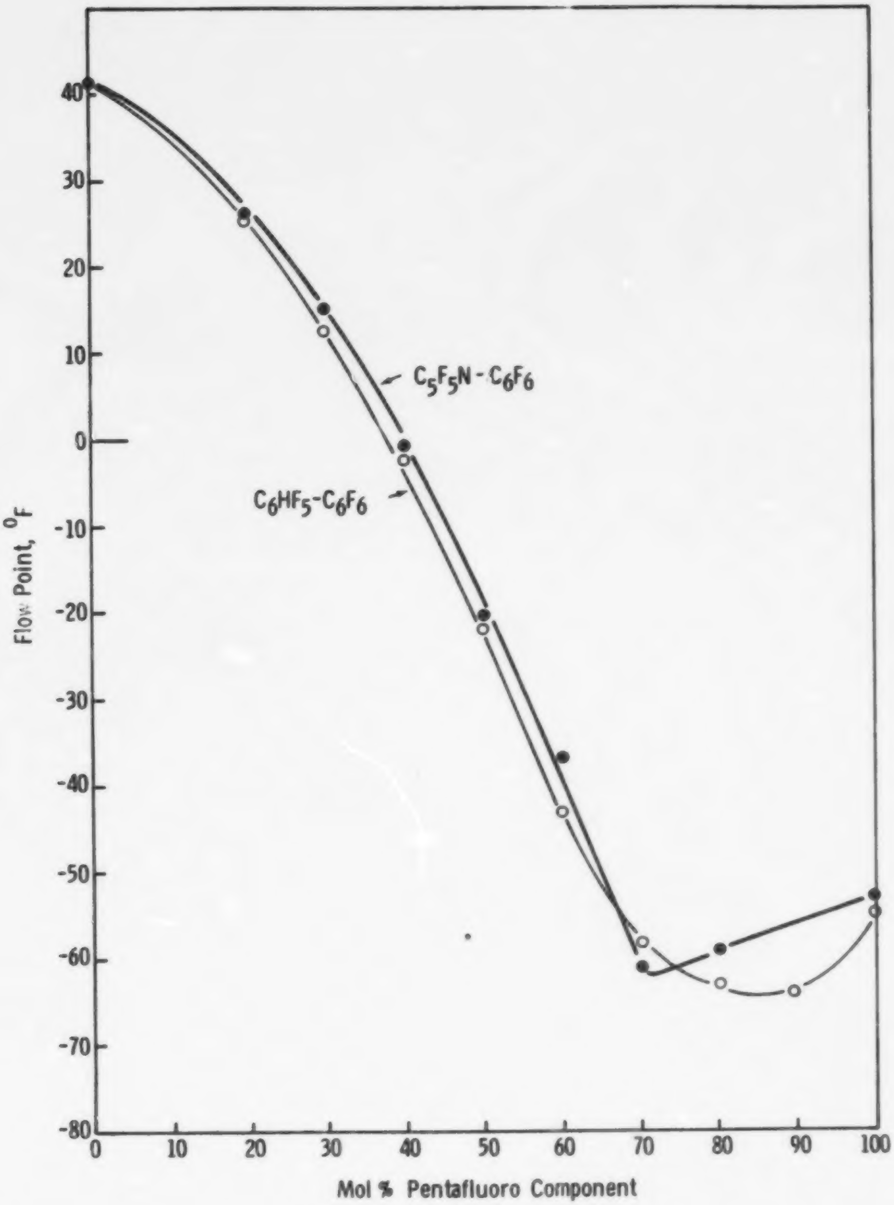

Figure 32. Flow Points - Binary Fluoroaromatics

6.10 RANKINE CYCLE COMPUTATIONS (CRITERIA 6-9)

In order to investigate the utility of the various candidate fluids as Rankine cycle working fluids, and to test them against Criteria 6 through 9, standard cycle analyses were provided and performed. As presented in section 6.1.2, two particular cycles were defined which had in common the same fluid state conditions at expander and pump inlets. Beyond this, the "reference ideal cycle" assumed 100% mechanical efficiencies for expander and pump, zero pressure losses between expander and pump, and no limitation on the extent of heat exchange surface available in the regenerator. In the "equivalent real cycle", expander and pump efficiencies were assumed to be 75%, representative pressure losses were assumed (section 6.1.2.2) in the various components between expander and pump, and a realistic limit was imposed (section 6.1.2.5) on the extent of regenerator heat exchange surface. In both cycles it was assumed that the expander and pump operated adiabatically.

The particular definition of cycle efficiency used throughout is:

$$\text{Cycle efficiency} = \frac{\text{Net indicated work out (W)}}{\text{Net indicated heat in (Q)}}$$

where W = the algebraic sum of the enthalpy changes across expander and pump (with appropriate sign change)

Q = the enthalpy rise across the vapor generator only

The limitation imposed on the regenerator size in the equivalent real cycle was actually a ceiling on the value of its UAk product (overall heat transfer coefficient times exchange surface area times cross-flow factor) of 125 Btu/HP-hr-°F.

A detailed description of the computational methods is given in Appendix Q.

6.10.1 Results of Computations

Mixed fluid cycle calculations were carried out by the desk calculator-program E-1393 interaction described in Appendix Q. Simple fluid (single component) cycle calculations were made using a Monsanto proprietary "Cycle Trace Program". The latter employs the Hirschfelder-Buehler-McGee-Sutton (HBMS) equation of state (ref. 54), but the results are comparable to the Redlich-Kwong equation used in the mixture calculations.

Cycle computations for advanced candidates are given in section 5.4. Cycle calculations for other fluids are summarized in Tables 60 through 67. Unless otherwise designated, the Ideal Reference Cycle (R2) was used. Fluids identified by serial number in the tables are:

Table 60. REFERENCE IDEAL CYCLES - SIMPLE FLUIDS

WORKING FLUID NO.	23	24	35	46	60	70	73	76	78	90	107
REFERENCE	2080	2080	2080	11211	2080	2080	2081	2081	2080	12081	2081
EFFICIENCIES, %											
CYCLE	30.00	30.00	30.00	30.00	30.00	30.00	30.00	30.00	30.00	18.36	30.00
% OF CARNOT	71.44	71.44	71.44	71.44	71.44	71.44	71.44	71.44	71.44	43.73	71.44
CYCLE, 0 % RGN	21.77	21.05	21.10	18.18	21.05	26.97	23.85	23.33	27.27	18.36	20.78
100 % RGN	31.68	31.63	31.90	31.39	30.64	32.42	31.67	31.81	31.45	20.51	30.53
CARNOT	41.99	41.99	41.99	41.99	41.99	41.99	41.99	41.99	41.99	41.99	41.99
TEMPERATURE, MAX F	712.0	712.0	712.0	712.0	712.0	712.0	712.0	712.0	712.0	712.0	712.0
MIN F	220.0	220.0	220.0	220.0	220.0	220.0	220.0	220.0	220.0	220.0	220.0
PRESSURE, MAX PSIA	1000.4	1000.0	1000.0	1009.2	1000.4	823.4	1000.0	1000.7	1000.6	170.6	1000.5
MIN PSIA	23.64	28.47	25.94	30.51	28.18	4.18	12.28	29.45	10.54	17.26	28.16
PER 100 CYCLE HP											
FLUID RATE,LB/HR	4574.	4768.	3866.	7676.	6331.	2693.	3405.	3313.	2809.	1129.	7174.
ENG EXH,CFM	278.7	244.4	261.5	234.3	246.6	1036.8	469.5	221.6	484.5	437.4	247.4
PUMP IN, GPM	11.11	12.16	11.65	10.80	13.24	6.15	10.68	10.47	6.26	2.32	15.04
ENGINE HP, GROSS	106.2	106.6	106.5	106.1	107.2	102.9	106.0	105.8	103.6	100.2	107.7
PUMP HP	6.15	6.59	6.45	6.06	7.19	2.92	6.01	5.77	3.61	0.20	7.71
HEAT FLOWS											
HEATER KBTU/HR	848.7	848.7	848.7	848.7	848.7	848.7	848.7	848.7	848.7	1386.6	848.7
REGEN KBTU/HR	320.7	361.1	358.2	551.8	361.0	95.4	219.0	242.8	85.1	0.0	376.6
CONDEN KBTU/HR	594.1	594.1	594.1	594.1	594.1	594.1	594.1	594.1	594.1	1131.9	594.1
WITHOUT REGEN											
HEATER KBTU/HR	1169.4	1209.8	1206.9	1400.6	1209.7	944.1	1067.7	1091.6	933.8	1386.6	1225.3
CONDEN KBTU/HR	914.8	955.2	952.3	1145.9	955.1	689.5	813.1	836.9	679.2	1131.9	970.7
ENGINE, % EFFIC =	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
PRESSURE RATIO	42.30	35.13	38.55	32.77	35.49	196.43	81.46	33.96	94.88	9.87	35.48
DENSITY RATIO	54.61	43.67	46.61	40.30	42.37	338.06	145.88	40.28	145.06	5.77	41.62
ISENTROPIC (1)	54.61	43.67	46.61	40.30	42.37	338.06	145.88	40.28	145.06	********	41.62
EXHAUST QUAL, %	168.1	175.1	177.7	208.7	167.4	130.5	149.2	154.6	123.1	100.0	167.1
DELTA -H, BTU/LB	59.09	56.92	70.11	35.18	43.11	97.31	79.27	81.28	93.90	226.02	38.23
ISENTROPIC	59.09	56.92	70.11	35.18	43.11	97.31	79.27	81.28	93.90	226.02	38.23
KAPPA (2)	0.936	0.942	0.951	0.944	0.953	0.907	0.883	0.954	0.915	1.307	0.957
NOZZLES, COEFF =	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
V SPOUT, FPS	1720.	1688.	1873.	1327.	1469.	2207.	1992.	2017.	2166.	3363.	1383.
MACH NO. SPOUT	2.67	2.60	2.63	2.57	2.61	3.21	2.84	2.60	2.95	2.15	2.61
A THROAT (3)	0.040	0.042	0.037	0.054	0.049	0.031	0.030	0.036	0.028	********	0.052
REGEN, % EFFECT =	87.69	89.20	87.63	93.61	95.30	60.06	83.00	83.40	68.50	0.00	97.59
Q, KBTU/CHP-HR	320.7	361.1	358.2	551.8	361.0	95.4	219.0	242.8	85.1	0.0	376.6
UA,KBTU/CHP-HR-F	5.687	6.544	5.810	11.876	9.398	1.239	4.125	3.826	1.605	0.000	12.547
DELTA T (LM), F	56.4	55.2	61.7	46.5	38.4	77.0	53.1	63.5	53.0	0.0	30.0
NTU (OG)	3.83	4.21	3.79	6.04	6.27	1.21	3.05	2.99	1.63	0.00	8.24
I-FACTOR	0.713	0.699	0.653	0.542	0.762	0.892	0.747	0.852	0.976	3.341	0.750
AT T, F, =	220.0	220.0	220.0	220.0	220.0	220.0	220.0	220.0	220.0	220.0	220.0
PUMP, % EFFIC =	99.99	99.94	99.95	100.04	100.01	99.96	100.18	100.05	100.19	101.72	99.95
PRESSURE RATIO	42.31	35.12	38.53	32.78	35.50	196.77	81.39	33.96	94.94	9.66	35.50

NOTES- (1) FROM ENGINE INLET TO EXHAUST ENTHALPY
(2) AVG ISENTROPIC EXPONENT, ENGINE IN TO EXH PRESS
(3) SQ IN (COMBINED) PER 100 CYCLE HP

Table 61. EQUIVALENT REAL CYCLES - SIMPLE FLUIDS

WORKING FLUID NO.	23	24	35	46	60	70	73	76	78	90	107
REFERENCE	2080	2080	2080	11211	2080	2080	2081	2081	2080	12051	2081
EFFICIENCIES, %											
CYCLE	22.25	21.97	22.15	20.67	21.23	24.77	22.72	22.76	23.72	13.41	20.86
% OF CARNOT	53.00	52.08	52.74	49.21	50.56	58.98	54.12	54.26	56.48	31.94	49.67
CYCLE, 0 % RGN	14.41	13.81	13.88	11.95	13.72	18.89	15.95	15.47	18.83	13.41	13.47
100 % RGN	23.24	23.05	23.26	22.91	22.10	25.02	23.39	23.46	23.89	14.89	21.78
CARNOT	41.99	41.99	41.99	41.99	41.99	41.99	41.99	41.99	41.99	41.99	41.99
TEMPERATURE, MAX F	712.0	712.0	712.0	712.0	712.0	712.0	712.0	712.0	712.0	712.0	712.0
MIN F	220.0	220.0	220.0	220.0	220.0	220.0	220.0	220.0	220.0	220.0	220.0
PRESSURE, MAX PSIA	1150.2	1149.7	1150.0	1150.2	1150.4	945.9	1149.5	1149.5	1149.0	228.5	1150.3
MIN PSIA	23.64	28.47	25.94	30.51	28.18	4.18	12.28	29.45	10.54	17.26	28.18
PER 100 CYCLE HP											
FLUID RATE,LB/HR	6961.	7322.	5919.	11744.	9792.	3860.	5129.	5032.	4089.	1548.	11163.
ENG EXH,CFM	362.6	319.9	341.0	302.4	325.7	1303.0	608.6	303.4	623.4	582.2	323.9
PUMP IN, GPM	16.91	18.67	17.84	16.53	20.48	8.81	16.09	15.89	9.11	3.18	23.40
ENGINE HP, GROSS	114.3	115.5	115.2	114.3	117.0	106.4	113.9	113.4	108.0	100.5	118.3
PUMP HP	14.34	15.49	15.17	14.27	17.02	6.42	13.86	13.42	8.05	0.52	18.33
HEAT FLOWS											
HEATER KBTU/HR	1144.2	1164.4	1149.7	1232.1	1199.2	1028.0	1120.5	1117.5	1073.6	1898.6	1220.7
REGEN KBTU/HR	622.8	679.8	684.6	898.0	656.7	319.6	475.7	528.4	278.6	0.0	670.0
CONDEN KBTU/HR	889.5	909.7	895.1	977.5	944.5	773.4	865.9	862.9	818.9	1644.0	966.1
WITHOUT REGEN											
HEATER KBTU/HR	1767.0	1894.2	1834.3	2130.1	1855.9	1347.6	1596.1	1645.9	1352.2	1898.6	1890.7
CONDEN KBTU/HR	1512.4	1589.5	1579.7	1875.5	1601.3	1093.0	1341.5	1391.3	1097.6	1644.0	1636.0
ENGINE, % EFFIC =	75.00	75.00	75.00	75.00	75.00	75.00	75.00	75.00	75.00	75.00	75.00
PRESSURE RATIO	34.39	28.56	31.34	26.65	28.85	159.69	66.23	27.61	77.14	9.24	28.85
DENSITY RATIO	46.68	37.22	39.69	33.99	36.20	296.44	125.52	34.72	128.23	6.46	35.56
ISENTROPIC (1)	19.50	16.21	16.97	15.15	15.67	83.57	46.41	15.06	43.46	3.29	15.37
EXHAUST QUAL, %	181.0	188.2	190.5	221.6	180.3	142.9	161.6	167.7	135.1	105.5	179.9
DELTA -H, BTU/LB	41.82	40.16	49.54	24.77	30.43	70.19	56.52	57.39	67.27	165.39	26.99
ISENTROPIC	55.76	53.55	66.06	33.03	40.57	93.58	75.36	76.52	89.70	220.52	35.99
KAPPA (2)	0.931	0.937	0.946	0.939	0.948	0.902	0.876	0.949	0.909	1.306	0.953
NOZZLES, COEFF =	0.950	0.950	0.950	0.950	0.950	0.950	0.950	0.950	0.950	0.950	0.950
V SPOUT, FPS	1608.	1575.	1748.	1234.	1371.	2093.	1871.	1886.	2051.	3251.	1291.
MACH NO. SPOUT	2.47	2.41	2.44	2.38	2.41	3.01	2.64	2.41	2.76	2.03	2.42
A THROAT (3)	0.068	0.072	0.063	0.091	0.083	0.054	0.056	0.060	0.048	0.188	0.089
REGEN, % EFFECT =	92.74	91.92	92.53	88.14	93.31	96.90	93.69	94.70	97.24	0.00	92.86
Q, KBTU/CHP-HR	622.8	679.8	684.6	898.0	656.7	319.6	475.7	528.4	278.6	0.0	670.0
UA,KBTU/CHP-HR-F	12.499	12.501	12.499	12.500	12.500	12.502	12.499	12.501	12.502	0.000	12.501
DELTA T (LM), F	49.8	54.4	54.8	71.8	52.5	25.6	38.1	42.3	22.3	0.0	53.6
NTU (OG)	5.44	5.14	5.24	4.09	5.25	8.47	6.02	6.32	8.58	0.00	5.14
I-FACTOR	0.671	0.661	0.608	0.522	0.721	0.820	0.693	0.796	0.901	3.157	0.714
AT T, F, =	248.0	248.0	248.0	248.0	248.0	248.0	248.0	248.0	248.0	248.0	248.0
PUMP, % EFFIC =	74.99	75.04	74.97	75.00	75.04	74.97	74.99	75.02	75.05	75.27	75.06
PRESSURE RATIO	48.65	40.39	44.33	37.70	40.83	226.04	93.64	39.04	109.02	13.24	40.92

NOTES- (1) FROM ENGINE INLET TO EXHAUST ENTHALPY
(2) AVG ISENTROPIC EXPONENT, ENGINE IN TO EXH PRESS
(3) SQ IN (COMBINED) PER 100 CYCLE HP

Table 62. REFERENCE IDEAL CYCLES, MFSN-15, PYRIDINE-WATER

Mol Fraction Pyridine	0.4	0.5	0.6	0.7	0.8	0.9
Efficiencies, %						
Cycle, Regen	27.38	27.80	28.33	28.93	29.30	30.71
% of Carnot	65.21	66.18	67.46	68.90	69.76	73.12
Cycle, Nonregen	26.64	26.31	26.18	26.17	25.85	26.87
% of Carnot	63.42	62.63	62.34	62.30	61.55	64.00
Carnot	42.00	42.00	42.00	42.00	42.00	42.00
Temperature, Max F	712	712	712	712	712	712
Min F	220	220	220	220	220	220
Pressure, Max psia	1,000	1,000	1,000	1,000	1,000	1,000
Min psia	21.29	20.67	19.60	18.05	16.03	13.55
Per 100 Cycle HP						
Fluid Rate, lb/hr	1,685.5	1,894.36	2,085.14	2,265.38	2,475.53	2,566.77
Eng Exh. CFM	248.03	264.23	281.79	305.84	348.64	393.34
Pump In, GPM	3.768	4.261	4.722	5.163	5.673	5.909
Engine HP	102.60	102.90	103.15	103.34	103.53	103.53
Pump HP	2.60	2.90	3.15	3.34	3.53	3.53
Regen Cycle*						
Regen KBTU/hr	26.18	51.87	73.74	93.17	115.91	118.16
Heater KBTU/hr	929.25	915.62	898.26	879.46	868.64	828.70
Conden KBTU/hr	674.74	661.11	643.75	624.95	614.13	574.19
Nonregen Cycle						
Heater KBTU/hr	955.43	967.49	972.00	972.63	984.55	946.86
Conden KBTU/hr	700.92	712.98	717.50	718.12	730.04	692.35
Engine, Effic %	100	100	100	100	100	100
Pressure Ratio	46.97	48.38	51.03	55.40	62.39	73.78
Density Ratio	36.27	41.00	47.05	55.72	69.62	93.45
Exhaust Qual %	103.88	107.93	111.46	114.91	118.87	120.58
Intake Qual %	--	--	--	--	--	--
Delta H, BTU/lb	-154.92	-138.25	-125.90	-116.10	-106.44	-102.67
Pump, Effic %	100	100	100	100	100	100
Pressure Ratio	46.97	48.38	51.03	55.40	62.39	73.78
Density Ratio	1.0034	1.0020	1.0025	1.0030	1.0035	1.004
I-Factor at T min	1.663	1.4780	1.329	1.205	1.071	1.020
Regen 30% Cyc Eff						
Effectiveness, %						83.36
Q, KBTU/CHP-Hr						98.50
UA, BTU/HP-Hr-F						206.34
Del T (LM), F						47.74
NTU(OG)						2.445

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*100% Effective Regenerator

Table 63. REFERENCE IDEAL CYCLES, 3-METHYLPYRIDINE, WATER MIXTURE, MFSN-21

Mol Fraction 3-Methylpyridine	0.3	0.3**	0.4	0.4**	0.5	0.5**	0.6	0.6**
Efficiencies, %								
Cycle, Regen	27.27	28.49	27.35	29.17	27.45	29.12	27.68	30.09
% of Carnot	64.93	67.83	65.12	69.46	65.37	69.33	65.92	71.65
Cycle, Nonregen	26.97	26.97	26.21	28.21	25.55	25.55	25.09	25.09
% of Carnot	64.22	64.22	62.40	62.40	60.83	60.83	59.74	59.74
Carnot	42.00	42.00	42.00	42.00	42.00	42.00	42.00	42.00
Temperature, Max F	712	712	712	712	712	712	712	712
Min F	220	220	220	220	220	220	220	220
Pressure, Max psia	1,000	1,000	1,000	1,000	1,000	1,000	1,000	1,000
Min psia	19.29	19.29	18.74	18.74	17.60	17.60	15.89	15.89
Per 100 Cycle HP								
Fluid Rate, lb/hr	1560.0	1560.0	1803.21	1803.21	2040.7	2040.7	2266.15	2266.15
Eng Exh. CFM	263.65	263.65	283.88	283.88	309.71	309.71	345.63	345.63
Pump In, GPM	3.401	3.401	3.962	3.962	4.530	4.530	5.082	5.082
Engine HP	102.40	102.40	102.76	102.76	103.11	103.11	103.43	103.42
Pump HP	2.40	2.40	2.76	2.76	3.11	3.11	3.43	3.43
Regen Cycle*								
Regen KBTU/hr	10.32	50.26	40.57	98.69	69.13	122.09	95.18	168.65
Heater KBTU/hr	933.25	893.31	930.49	872.37	927.03	874.08	919.18	847.41
Conden KBTU/hr	678.70	647.76	675.98	617.86	672.51	619.56	664.68	591.21
Nonregen Cycle								
Heater KBTU/hr	943.57	943.57	971.07	971.07	996.16	996.16	1014.37	1014.37
Conden KBTU/hr	689.02	689.02	716.56	716.56	741.65	741.65	759.86	759.86
Engine, Effic %	100	100	100	100	100	100	100	100
Pressure Ratio	51.84	51.84	53.37	53.37	56.81	56.81	62.93	62.93
Density Ratio	39.07	39.07	45.12	45.12	53.22	53.22	65.36	65.36
Exhaust Qual %	101.52	101.52	106.01	106.01	110.28	110.28	114.32	114.32
Intake Qual %	--	--	--	--	--	--	--	--
Delta H, BTU/lb	-167.06	-167.06	-145.04	-145.04	-124.72	-124.72	-112.31	-112.31
Pump, Effic %	100	100	100	100	100	100	100	100
Pressure Ratio	51.84	51.84	53.37	53.37	56.81	56.81	62.93	62.93
Density Ratio	1.0006	1.0006	1.0007	1.0007	1.0009	1.0009	1.0012	1.0012
I-Factor at T min	1.749	1.749	1.531	1.531	1.350	1.350	1.205	1.205

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*100% Effective Regenerator
**Condensation in Regenerator

Table 64. REFERENCE IDEAL CYCLES, 2-METHYLPYRIDINE, WATER MIXTURE, MFSN-23

Mol Fraction 2-Methylpyridine	0.2	0.3	0.4	0.5	0.6	0.7
Efficiencies, %						
Cycle, Regen	NA	27.93	28.06	28.07	27.91	27.81
% of Carnot		66.50	66.81	66.83	66.45	66.22
Cycle, Nonregen	26.97	26.85	25.88	25.01	24.09	23.36
% of Carnot	64.21	63.92	61.61	59.54	57.36	55.61
Carnot	42.00	42.00	42.00	42.00	42.00	42.00
Temperature, Max F	712	712	712	712	712	712
Min F	220	220	220	220	220	220
Pressure, Max psia	893.37	1000.	1000.	1000.	1000.	1000.
Min psia	22.76	22.76	22.70	22.38	21.59	20.17
Per 100 Cycle HP						
Fluid Rate, lb/hr	1375.51	1619.85	1969.71	2170.3	2456.2	2742.6
Eng Exh. CFM	220.51	228.44	242.50	254.72	271.42	295.21
Pump In, GPM	3.04	3.609	4.291	4.982	5.721	6.468
Engine HP	101.79	102.31	102.75	103.17	103.59	103.95
Pump HP	1.79	2.31	2.75	3.17	3.59	3.95
Regen Cycle*						
Regen KBTU/hr		35.356	76.53	111.09	144.58	174.56
Heater KBTU/hr	NA	911.26	907.05	906.72	911.86	915.12
Conden KBTU/hr		657.47	652.54	652.21	657.35	660.01
Nonregen Cycle						
Heater KBTU/hr	943.7	946.62	982.58	1017.81	1056.44	1089.67
Conden KBTU/hr	650.94	692.11	729.77	763.30	801.93	835.17
Engine, Effic %	100	100	100	100	100	100
Pressure Ratio	39.255	43.93	44.05	44.69	46.32	49.59
Density Ratio	26.327	33.78	38.00	42.82	49.39	59.79
Exhaust Qual %	100	105.53	111.72	117.03	121.99	126.42
Intake Qual %	--	--	--	--	--	--
Delta H, BTU/lb	-373.23	-160.75	-132.76	-120.99	-107.34	-96.47
Pump, Effic %	100	100	100	100	100	100
Pressure Ratio	39.255	43.93	44.05	44.69	46.32	49.59
Density Ratio	1.0002	1.0011	1.0013	1.0017	1.0021	1.0027
I-Factor at T min	1.985	1.480	1.190	1.0046	0.8854	0.7857
Regen 30% Cyc Eff	NA					
Effectiveness, %	NA	>100	>100	>100	>100	>100
Q, KBTU/CHP-Hr	NA	NA	NA	NA	NA	NA
UA, BTU/HP-Hr-F	NA	NA	NA	NA	NA	NA
Del T (LM), F	NA	NA	NA	NA	NA	NA
NTU(OG)	NA	NA	NA	NA	NA	NA

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*100% Effective Regenerator

Table 65. REFERENCE IDEAL CYCLES, 4-METHYLPYRIDINE, WATER MIXTURE, MFSN-24

Mol Fraction 4-Methylpyridine	0.3	0.4	0.5	0.6	0.7	0.8
Efficiencies, %						
Cycle, Regen	27.55	28.06	28.37	28.62	28.61	28.52
% of Carnot	65.60	66.81	67.54	68.14	68.13	67.91
Cycle, Nonregen	27.46	27.13	26.68	26.23	25.85	25.55
% of Carnot	65.38	64.60	63.53	62.45	61.55	60.83
Carnot	42.00	42.00	42.00	42.00	42.00	42.00
Temperature, Max F	712	712	712	712	712	712
Min F	220	220	220	220	220	220
Pressure, Max psia	1,000	1,000	1,000	1,000	1,000	967.73
Min psia	18.86	17.81	16.26	14.33	12.16	9.653
Per 100 Cycle HP						
Fluid Rate, lb/hr	1,577.81	1,818.77	2,055.59	2,289.28	2,531.5	2,799.2
Eng Exh. CFM	269.16	295.84	330.09	376.60	444.04	552.58
Pump In, GPM	3.535	4.116	4.703	5.289	5.897	6.563
Engine HP	102.57	102.78	103.01	103.26	103.53	103.74
Pump HP	2.57	2.78	3.01	3.26	3.53	3.74
Regen Cycle*						
Regen KBTU/hr	3.11	31.04	56.67	79.06	95.00	103.92
Heater KBTU/hr	923.71	907.00	897.23	889.35	889.48	892.32
Conden KBTU/hr	669.20	652.49	642.73	636.73	634.97	637.81
Nonregen Cycle						
Heater KBTU/hr	926.82	938.04	953.91	968.41	984.48	996.23
Conden KBTU/hr	672.31	683.54	699.40	715.79	729.97	741.73
Engine, Effic %	100	100	100	100	100	100
Pressure Ratio	53.03	56.15	61.50	69.79	82.30	100.24
Density Ratio	40.09	48.01	59.09	76.36	108.13	170.38
Exhaust Qual %	100.46	104.76	108.82	112.42	114.96	116.29
Intake Qual %	--	--	--	--	--	--
Delta H, BTU/lb	-165.45	-143.83	-127.53	-114.79	-104.09	-94.32
Pump, Effic %	100	100	100	100	100	100
Pressure Ratio	53.03	56.15	61.5	69.79	82.3	100.24
Density Ratio	1.0012	1.0014	1.0017	1.028	1.0027	1.0031
I-Factor at T min	1.728	1.510	1.342	1.203	1.091	1.001

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*100% Effective Regenerator

Table 66. SPECIAL IDEAL CYCLES, 2-METHYLPYRIDINE, WATER MIXTURE, MFSN-23

Mol Fraction 2-Methylpyridine	0.4(a)	0.4(b)	0.4(c)	1.0(d)	0.0(e)
Efficiencies, %					
Cycle, Regen	NA	30.48	30.05	29.33	NA
% of Carnot	NA	66.20	66.36	69.83	NA
Cycle, Nonregen	26.99	26.49	26.41	23.33	19.02
% of Carnot	64.28	57.53	58.33	55.56	45.29
Carnot	42.00	46.04	45.28	42.00	42.00
Temperature, Max F	712	800	782.5	712	712
Min F	220	220	220	220	220
Pressure, Max psia	1,784.9	1,000	1,000	1,000	172.7
Min psia	22.70	22.70	22.70	10.92	17.28
Per 100 Cycle HP					
Fluid Rate, lb/hr	2,001.97	1,688.42	1,724.08	3,497.0	1,123.1
Eng Exh. CFM	220.65	239.62	239.91	537.3	449.9
Pump In, GPM	4.525	3.816	3.897	8.456	2.646
Engine HP	105.23	102.44	102.50	104.50	100.24
Pump HP	5.23	2.44	2.50	4.50	0.239
Regen Cycle*					
Regen KBTU/hr	NA	126.01	116.59	221.71	NA
Heater KBTU/hr	NA	834.83	847.08	867.80	NA
Conden KBTU/hr	NA	580.32	592.58	614.48	NA
Nonregen Cycle					
Heater KBTU/hr	942.70	960.84	963.68	1,090.69	1,338.0
Conden KBTU/hr	688.19	706.33	709.17	836.18	1,083.5
Engine, Effic %	100	100	100	100	100
Pressure Ratio	78.62	44.05	44.05	91.61	9.991
Density Ratio	82.06	36.63	36.84	191.21	5.857
Exhaust Qual %	100	121.71	119.67	137.20	100
Intake Qual %	--	--	--	--	--
Delta H, BTU/lb	-133.78	-154.42	-151.31	-76.05	-227.2
Pump, Effic %	100	100	100	100	100
Pressure Ratio	78.62	44.05	44.05	91.61	5.857
Density Ratio	1.0023	1.0013	1.0013	1.0041	1.0003
I-Factor at T min	1.190	1.190	1.190	0.588	3.192
Regen 30% Cyc Eff					
Effectiveness, %	NA	89.26	100	>100	NA
Q, KBTU/CHP-Hr	NA	112.48	116.59		NA
UA, BTU/HP-Hr-F	NA	1,926.4	∞		NA
Del T (LM), F	NA	58.38	0		NA
NTU(OG)	NA	2.854	∞		NA

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* 100% effective regenerator

(a) 1000 psi pressure maximum restraint omitted

(b) 800°F temperature allowed in gas generator

(c) Upper temperature adjusted for 30% cycle efficiency

(d) Pure component, 2-methylpyridine

(e) Pure component, water

Table 67. SPECIAL IDEAL CYCLES, 4-METHYLPYRIDINE, WATER

Cycle Description and m.f. Organic	0.3**	0.3‡	0.6**
Efficiencies, %			
Cycle, Regen	28.89	26.95	32.06
% of Carnot	68.78	64.17	76.32
Cycle, Nonregen	27.46	26.03	26.23
% of Carnot	65.38	61.97	62.45
Carnot	42.00	42.00	42.00
Temperature, Max F	712	712	712
Min F	220	220	220
Pressure, Max psia	1,000	900	1,000
Min psia	18.86	18.86	14.33
Per 100 Cycle HP			
Fluid Rate, lb/hr	1,577.81	1,626.54	2,289.3
Eng Exh. CFM	269.16	300.19	376.6
Pump In, GPM	3.535	3.644	5.289
Engine HP	102.57	101.84	103.26
Pump HP	2.57	1.84	3.26
Regen Cycle*			
Regen KBTU/hr	82.53	33.51	176.35
Heater KBTU/hr	844.29	944.38	792.05
Conden KBTU/hr	589.78	689.87	539.43
Nonregen Cycle			
Heater KBTU/hr	926.82	977.90	968.41
Conden KBTU/hr	672.31	723.39	715.79
Engine, Effic %	100	100	100
Pressure Ratio	53.03	37.12	69.79
Density Ratio	40.09	28.04	76.36
Exhaust Qual %	100.46	104.85	112.42
Intake Qual %	--	--	--
Delta H, BTU/lb	-165.45	-159.35	-114.79
Pump, Effic %	100	100	100
Pressure Ratio	53.03	37.12	69.79
Density Ratio	1.0012	1.0008	1.028
I-Factor at T min	1.728	1.728	1.203

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* 100% effective regenerator
** Condensation in regenerator
‡ Lower pressure in boiler

23	p-difluorobenzene
24	m-difluorobenzene
35	fluorobenzene
46	hexafluorobenzene
60	1,2,3,5-tetrafluorobenzene
70	3-methylpyridine
73	toluene
76	benzene
78	pyridine
90	water
107	pentafluoropyridine

Reference ideal cycles calculated for many of the Table 60-67 candidates are extracted in Table 68. The first column is a test of Criterion 6, which requires an ideal cycle efficiency of at least 30% at any level of regenerator effectiveness. All straight organic fluids pass, whereas the pyridine-water mixtures fail. While water itself appears disqualified, it is capable of higher efficiencies by raising its upper operating temperature.

Other entries in the table demonstrate compliance with certain interim (non-criterion) goals; namely,

1. condenser pressure from 5 to 50 psia
2. ideal expansion density ratio less than about 40 (to serve in a single expansion reciprocator)
3. ideal expansion enthalpy drop less than about 200 Btu/pound (to serve in a single-stage impulse turbine)
4. I-factor in the approximate range of 0.65 to ∞ (components) or 0.75 to 1.5 (final fluids)

Equivalent Real Cycle calculations employing many of the same simple fluids recorded in Table 68 are extracted in Table 69. Comparison of the entries with the reciprocating/turbine suitability Criteria 8 and 9 reveals all fluoroaromatics and benzene suitable for either engine type and all aromatics but benzene suited only for turbine use.

6.10.2 I-Factor as a Determinant of Cycle Efficiency

The data of Tables 60 and 61 permit an analysis of the efficacy of I-factor as a screening criterion. Referring first to the reference ideal cycle data of Table 60, in Figure 33 is plotted the regenerator UAk product (linked to regenerator size in section

Table 68. SUMMARY OF REFERENCE IDEAL CYCLE CALCULATIONS ON THERMALLY STABLE CANDIDATES

	Ideal Cycle Effic.(%)*	Condenser Pressure (psia)	Expansion Density Ratio	Expansion Enthalpy Drop (Btu/lb)	I-Factor at 220°F
Aromatics					
Benzene	31.8	29.4	40.3	81.3	0.85
Toluene	31.7	12.3	145.9	79.3	0.75
Pyridine	31.5	10.5	145.1	93.9	0.98
3-Methylpyridine	32.4	4.2	338.1	97.3	0.89
Fluoro Aromatics					
Fluorobenzene	31.9	25.9	46.6	70.1	0.65
m-Difluorobenzene	31.6	28.5	43.7	56.9	0.70
p-Difluorobenzene	31.7	23.6	54.6	59.1	0.71
1,2,3,5-Tetrafluorobenzene	30.6	28.2	42.4	43.0	0.76
1,2,4,5-Tetrafluorobenzene	30.8	22.8	54.7	44.8	0.77
Pentafluorobenzene	30.3	26.6	45.2	35.3	0.68
Octafluorotoluene	30.2	14.9	86.9	29.7	0.55
Pentafluoropyridine	30.3	28.2	41.6	38.2	0.75
Hexafluorobenzene	31.4	30.5	40.3	35.2	0.54
Water	20.5	17.3	5.8	226.0	3.34
Pyridine/Water Solutions**					
40% Pyridine	27.4	21.3	36.3	154.9	1.66
60%	28.3	19.6	47.1	125.9	1.33
30% 2-Methylpyridine	27.9	22.8	33.8	160.8	1.48
60%	27.9	21.6	49.4	107.3	0.89
30% 3-Methylpyridine	27.3	19.3	39.1	167.1	1.75
60%	27.7	15.9	65.4	112.3	1.21
30% 4-Methylpyridine	27.6	18.9	40.1	165.5	1.73
60%	28.6	14.3	76.4	114.8	1.20

---

* Full regeneration on all simple fluids; full regeneration or regeneration only to the dew line, whichever occurs first, on all solutions.

** Concentrations shown are mol percents.

Table 69. SUMMARY OF EQUIVALENT REAL CYCLE CALCULATIONS ON SIMPLE THERMALLY STABLE FLUIDS[1]

	Real Cycle Effic.(%)[2]	Expansion	
		Density Ratio[3]	Enthalpy Drop (Btu/lb)
Aromatics			
benzene	22.8	15.1	57.4
toluene	22.7	46.4	56.5
pyridine	23.7	43.5	67.3
3-methylpyridine	24.8	83.6	70.2
Fluoro Aromatics			
fluorobenzene	22.1	17.0	49.5
m-difluorobenzene	21.9	16.2	40.2
p-difluorobenzene	22.3	19.5	41.8
1,2,3,5-tetrafluorobenzene	21.2	15.7	30.4
pentafluoropyridine	20.9	15.4	27.0
hexafluorobenzene	20.7	15.2	24.8

---

[1] Condenser pressures and 220°F. I-factors same as in Table 68.

[2] Regenerator Q/ΔT(log mean) = UAk = 125 Btu/HP-hr-°F.

[3] Isentropic, from engine inlet to exhaust enthalpy.

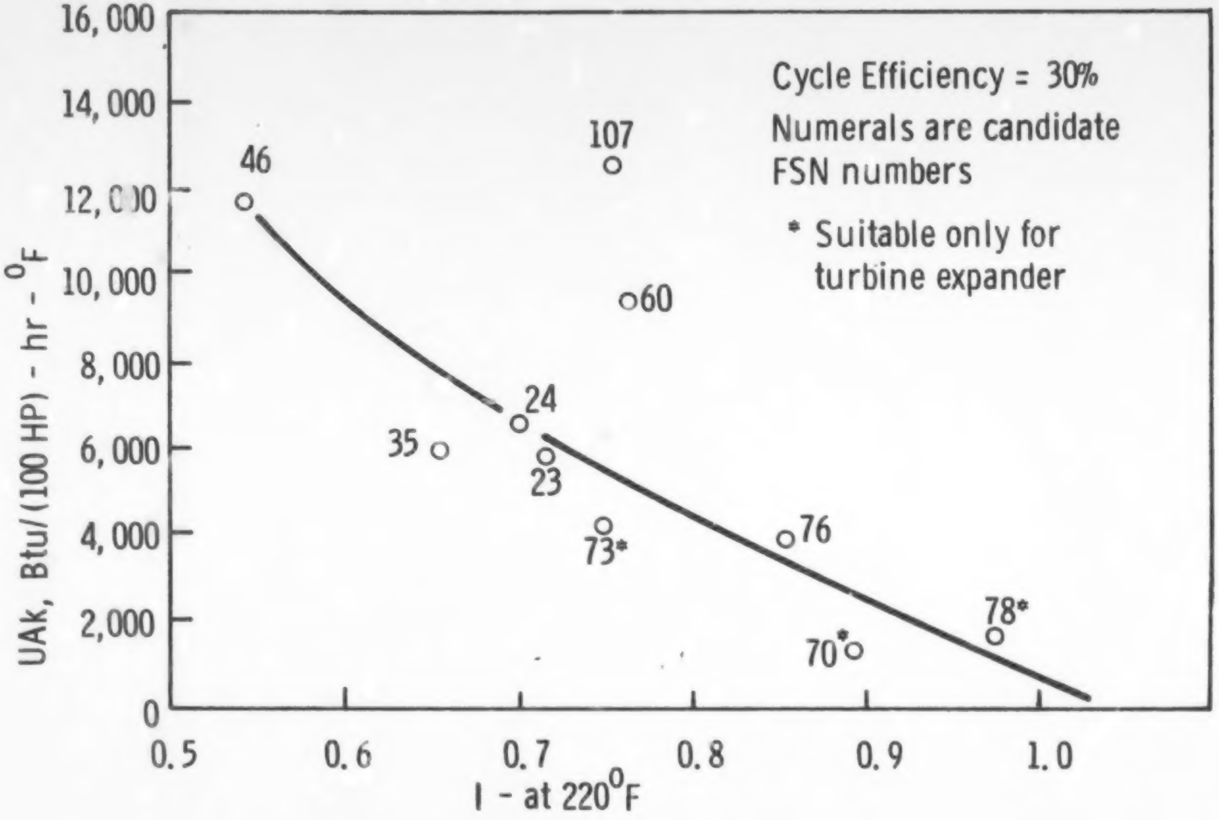

Figure 33. Reference Ideal Cycle Regenerator "Size" (UAk) as Affected by I-Factor

6.1.2.3) versus I-factor for nine simple fluids. This graph clearly reveals the expected trend to larger regenerator sizes with diminishing I-factor. It also reveals a fairly wide scatter, which argues against setting too narrow limits on an I-factor criterion.

As discussed at some length in sections 6.1.2.3-5, a regenerator sized to give a particular ideal cycle efficiency is likely to be far too small for the real cycle because of the much higher heat loads in the real system associated with the need to circulate considerably more fluid per net cycle horsepower. This argument lead to the concept of the equivalent real cycle. Using this cycle it is possible to show, with reasonable relation to reality, the relationship between cycle efficiency and I-factor when the regenerator "size" is held constant at its ceiling value.

The relationship is demonstrated in Figure 34 for the same nine fluids. Data were from Table 61. The general downward trend of cycle efficiency with decreasing I-factor is apparent despite a fairly wide scatter. This graph clearly presents the argument for a high I-factor fluid in the automotive application, where regenerator space is at a premium. It also buttresses the initial selection of I-factor criterion limits of 0.65 to 1.5.

Another presentation tending to support the validity of the I-factor screen is given in Figure 35. Here are plotted ideal cycle efficiencies versus I-factor for a large number of candidates, both simple and complex. Three different families of points resulted from the three different degrees of regeneration assumed, namely:

- 100% effective (curve 1)
- regeneration of vapor only to saturation (dewpoint)
- 0% effective

The gap between the 0 and 100% effectiveness curves is a qualitative indication of the size regenerator needed to achieve reasonable cycle efficiency. Data were from Tables 60 through 67.

An additional point of interest in Figure 35 is the fall-off in cycle efficiency associated with I-factors above 1.0. All the fluids in this range contain water. The reason for this fall-off is traceable to the fact that water, compared to the organics, has an unusually high critical pressure. At the 1000 psia maximum allowable fluid pressure, water boils at the unusually low temperature of 545°F. A large amount of the heat added to the water to bring it to the 712°F (167 degrees of superheat) peak cycle temperature is therefore added at temperatures far below 712°F. Besides leading to a lower cycle efficiency, this explains one of the reasons for the current interest in organic working fluids. Dilution of water with soluble organic fluids tends to improve

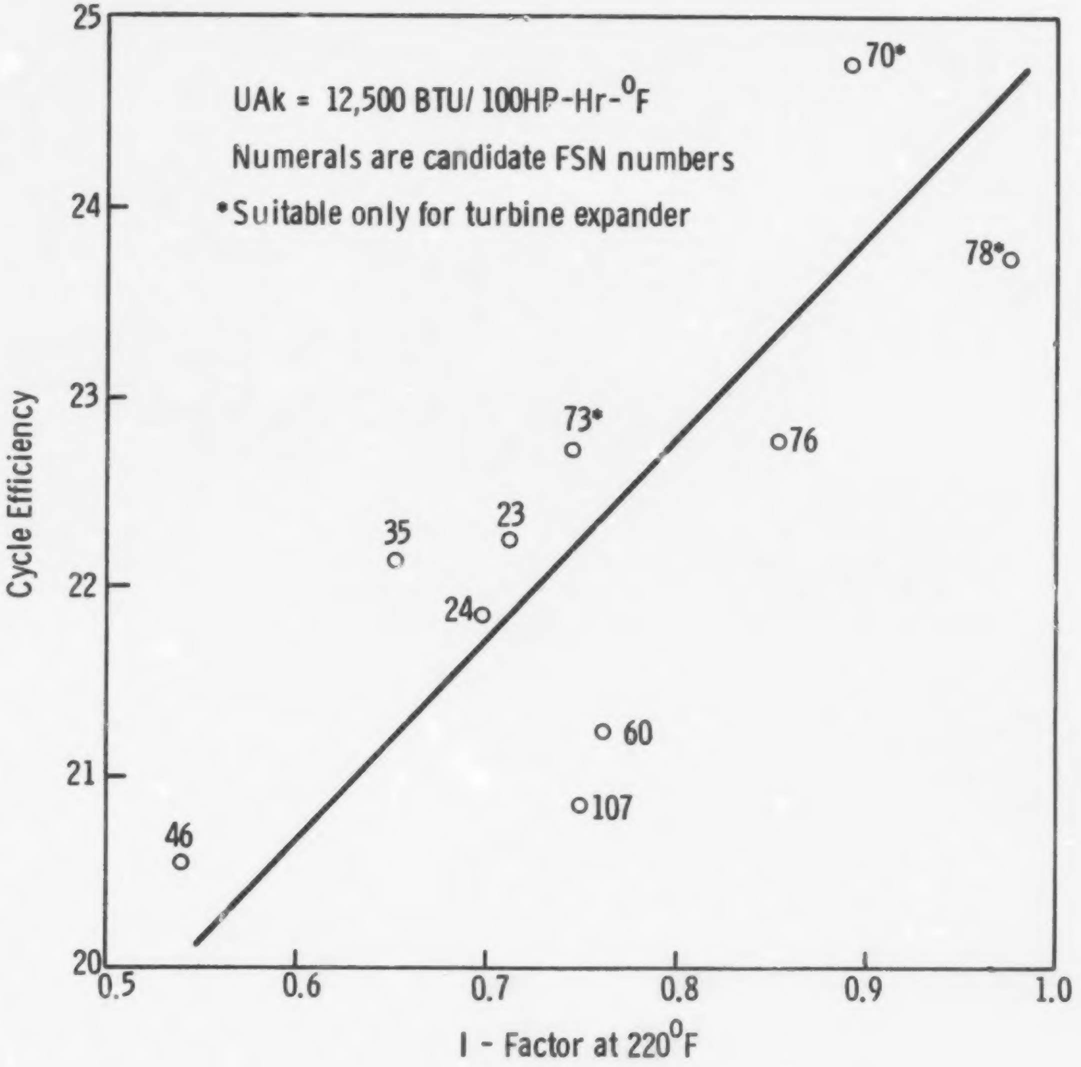

Figure 34. Equivalent Real Cycle Efficiency as Affected by I-Factor at Fixed Regenerator Size

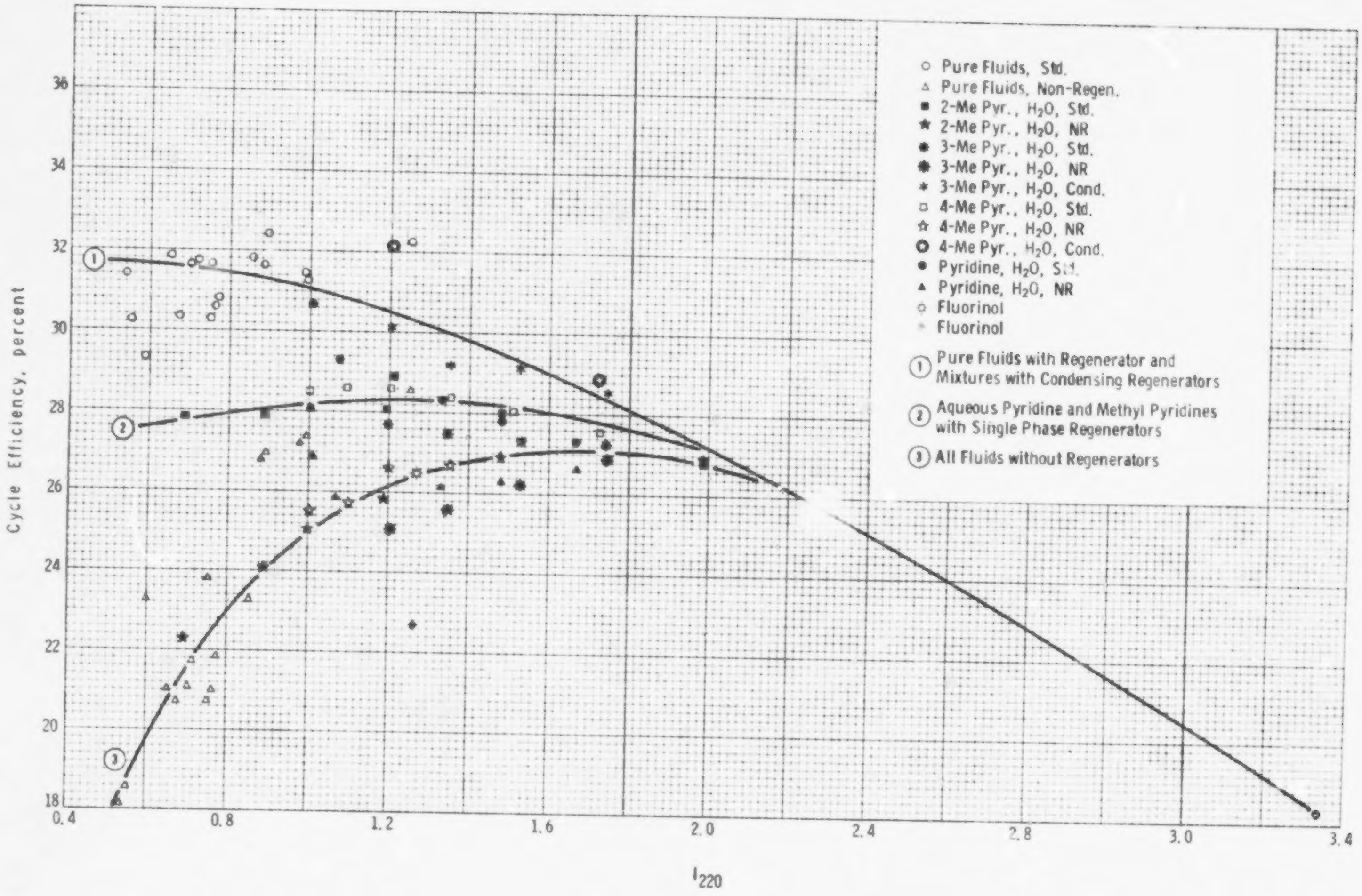

Figure 35. Correlation of Cycle Efficiencies of Candidate and Reference Fluids versus I-Factor

this situation by reducing the apparent critical pressure and the amount of superheat required.

6.11 SPECIAL STABILITY TEST WORK

Several limited thermochemical stability studies were made in areas slightly aside from the central objectives of the contract.

6.11.1 Fluorinol-85 Stability Investigations

Fluorinol-85 is an 85 mol percent mixture of 2,2,2-trifluoroethanol with 15 mol percent water manufactured by Halocarbons Incorporated. It is currently the design fluid for the automotive Rankine engine under development by Thermo Electron Corporation. Their maximum bulk fluid temperature is presently set at 550°F. The question inevitably arose as to the possibility of operating Fluorinol, along with its lubricant (a refrigeration oil) at a higher temperature. Accordingly, a series of ampoule tests were carried out on Fluorinol-85 at 600°F. As in the Criterion 5 ampoule tests, no attempt was made to remove freeboard air from the ampoules. Samples were run both in stainless steel and in the standard SAE 1008 low carbon steel ampoules. Both survived 336 hours at 600°F with no evidence of degradation aside from developing a straw yellow color. No strong acidity (HF) formed nor were significant changes in composition found, as evidenced by a gas-liquid chromatogram. These tests were repeated with various amounts (2%, 12% and 25%) of lubricating oil present. Again the appearance after 336 hours was quite good and it was concluded that Fluorinol-85 systems could probably be successfully operated at a 600°F boiler temperature provided hot-spot problems were minimal. In one experiment, a sample of Fluorinol-85 in a stainless steel ampoule was held at 600°F for 740 hours. At this point the fluid was still almost colorless but a test with moisture indicator paper suggested the presence of strong acid (presumably HF in small amounts).

Inasmuch as results at 600°F were encouraging, a series of Fluorinol-85 samples both with and without refrigeration oil were run at 660°F. The results indicated that Fluorinol-85/oil combinations were every bit as stable as Fluorinol-85 without oil. Samples containing no oil developed an unpleasant odor after 24 hours exposure and after 48 hours showed traces of weak acid as evidenced by the decolorization of aqueous bromophenol blue indicator solution. The quantity of weakly acidic material did not appreciably increase with time, and no strong acid could be detected up to 336 hours exposure. The use of stainless rather than mild steel tubes did not significantly change these results.

An identical series of samples containing 15% refrigeration oil did not develop odor nor give evidence of weak acid until about 144 hours. Again the weak acid did not increase significantly with time and no strong acid (HF) was detected at 336 hours. At

500 hours, however, some gas pressure remained in the cooled sample tubes and traces of strong acid were in evidence. The oil layer appeared light-colored and in reasonably good condition. Several modified versions of the basic refrigeration oil were also tested along with Fluorinol-85. Results indicated that all were about the same. This was not unexpected since all were hydrocarbon products of similar composition.

Some additional experiments were carried out to determine the effect of inerting the sample with nitrogen before thermal exposure. As discussed earlier, standard procedure had previously been to seal the Fluorinol-85 in the pressure tube without excluding ambient air. In connection with this investigation a simple procedure for detecting the weak acid formed was adopted. First, an indicator solution was prepared which consisted of 6 drops 0.04% bromophenol blue solution (Fisher Scientific Cat. No. 5-985-F) in 20 ml of distilled water. Under neutral conditions its color is light blue. Weak acid in exposed Fluorinol-85 samples is then measured by dropwise addition of test sample from a 0.25 ml graduated syringe to 2.0 ml of the indicator solution. The volume of sample required to discharge the blue color of the indicator provides a relative measure of the amount of weak acid present. Fresh Fluorinol-85 does not cause the blue color to change, thus the less sample required to cause the indicator to turn from blue to pale yellow, the more weak acid is present. The method is, however, somewhat imprecise since the acid being detected is quite weak. This causes the indicator color to fade over a range rather than change abruptly as it would under the influence of strong acid.

Results obtained on exposing Fluorinol-85 samples under nitrogen and with ambient air are summarized as follows:

Sample Sealed Under	Suniso 3GS Oil Present	Exposure Time at 660°F (hr)	Exposed Fluorinol-85 Required to Discharge Color in 2.0 ml Indicator Solution (ml)
Air	No	72	~0.1
N_2	No	72	~0.2
Air	Yes	168	~0.05
N_2	Yes	168	~0.05
Air	Yes	336	~0.05
N_2	Yes	336	~0.05

From these experiments it was concluded that at short exposure times nitrogen-inerting may be somewhat beneficial, but after long exposure in the presence of lubricant no significant advantage accrues from nitrogen-blanketing. It was also observed that samples at 168 hours or longer were under slight pressure when brought back to room temperature. This indicates the presence of some gaseous decomposition products, possibly of hydrogen formed by reaction of water with the iron ampoule surface. The identity of this gas was not established.

Because of the unexpectedly good stability of Fluorinol-85 and oil at 660°F additional experiments were carried out at 720°F. Results conformed closely with earlier observations at this temperature (see MFSN-20, Table 47). After 24 hours at 720°F a Fluorinol-85 + 15% refrigerant oil sample showed evidence of a small amount of gas but no acids, either weak or strong. Both the Fluorinol-85 and oil layers were relatively clean and showed little color change. After 48 hours, however, extensive decomposition was apparent. A heavy, black, dusty deposit had formed, and large amounts of strong acid were detectable. One may conclude from these results that Fluorinol-85 and hydrocarbon oils might function satisfactorily at ~660°F but have a fairly sharp break point around 700°F.

6.11.2 Nonvolatiles from Pyridine-Water Type Fluids

As thermal stability appeared to be the principal weakness of pyridine and methylpyridine-water fluids an effort was made to better judge the extent and seriousness of decomposition as observed in ampoule tests. This presents an experimental problem, since these fluids do not give an easily measured entity, such as formation of acid, by means of which the decomposition can be followed. Ultimately, the formation of nonvolatile tars was found to be a convenient means of following the decomposition process. Results of a series of experiments are summarized in Table 70.

The table shows that the results are not entirely consistent. In any event, formation of nonvolatiles remains fairly low in each of the fluids and shows no dramatic increase over the time interval studied. The appearance of the residues differed substantially. Thus the residues from pyridine and 4-methylpyridine-water solutions appeared as dry, finely divided brown solid whereas residue from the other methylpyridine solutions appeared as a semi-liquid tar.

6.11.3 Carboranes

Interest in the recently discovered class of chemical compounds called closo-carboranes (ref. 55) stems from the recognition that polyhedral carbon-boron "cage" molecules are relatively stable thermodynamically, some extremely so. While these compounds are currently laboratory curiosities, and, therefore, "unavailable" in a practical sense, there is some reason to believe they could be manufactured in large quantities at reasonable prices if a demand developed. Through the generosity of Professor M. F. Hawthorne, University of California, Los Angeles, small samples of

Table 70. FORMATION OF NONVOLATILE TARS IN METHYLPYRIDINE-WATER FLUIDS AFTER THERMAL EXPOSURE AT 720°F

Mixed Fluid No.	Composition 0.5-0.5 mol Fraction	Nonvolatile Materials* Produced (wt%) at 720°F after Various Exposure Times				
		48 hr	96 hr	168 hr	240 hr	264 hr
M-15	Pyridine/water	0.013	0.013	0.044	0.054	0.00
M-21	3-Methylpyridine/ water	0.0	0.080	0.018	0.148	0.475
M-23	2-Methylpyridine/ water	0.0	0.0	0.016	0.049	0.121
M-24	4-Methylpyridine/ water	0.125	0.033	0.051	0.545	0.286

---

*Procedure: A carefully weighed sample (approximately 1 g) of exposed fluid evaporated for 16 hours in an oven at 149°F. The residue remaining is reported as nonvolatile.

three substituted *closo*-carboranes were obtained for evaluation. The three were (ref. 55):

A. C,C'-dimethyl-2,4-$C_2B_5H_5$, or $(CH_3)_2B_5C_2H_5$

melting point	-29°C
boiling point	?
cage geometry	pentagonal bipyramid
references	56, 57
sample volume	1 ml

B. C,C'-dimethyl-1,7-$C_2B_6H_6$, or $(CH_3)_2B_6C_2H_6$

melting point	-40°C
boiling point	63°C @ 134 torr
cage geometry	dodecahedron
references	58, 59
sample volume	2 ml

C. C,C'-dimethyl-1,7-$C_2B_7H_7$, or $(CH_3)_2B_7C_2H_7$

melting point	-22°C
boiling point	?
cage geometry	tricapped trigonal prism
references	58, 59
sample volume	3 ml

While all three of these are known to be very thermally stable, their ability to resist ignition and burning is not well established. Flammability is thought to be the key issue in considering the carboranes as candidates, but the available samples fell far short of the amounts required for even flash and fire point measurement.

For these reasons, it was decided to commit the limited samples to microliter-scale tests of oxidation stability in side-by-side comparison with reference fluids of known flammability.

6.11.3.1 Oxygen Consumption Measurements - Method (ref. 60) - Thin wall borosilicate glass melting point tubes (Size D, 1 mm ID) were cut to a length of 47 mm. After the tubes were quickly cooled in dry ice, 1 µl of sample was injected into each tube with a 5 µl syringe. The tubes were sealed by fusing the open end with a natural gas-oxygen flame; the same amount of air was trapped in each tube. Control tubes containing air, but no sample, were prepared in the same manner.

All but two of the sealed tubes were placed in an electric furnace at 178°C (352°F). Duplicate tubes were removed from the furnace at intervals of 10, 30, and 60 minutes for gas chromatographic analyses of the residual O_2/N_2 ratio. Two sets of controls - (a) air with no sample and (b) air with sample, but not heated - were also analyzed.

The residual gases in the tubes were released into the injection port of a gas chromatograph by crushing the capsules with a solid sample injector. Analysis conditions were:

Instrument - F&M Model 700

Column - 9 ft x 1/4 in. stainless steel tubing packed with 100-120 mesh Molecular Sieve 5A

Column Oven Temperature - 110-120°C

Injection Port Temperature - 50°C

TC Detector Temperature - 180°C

TC Detector Current - 250 mA

Carrier Gas and Flow - He, 50 psig, 120 ml/min

Attenuation - X2 and X8

Ratios of the peak heights for O_2 and N_2 peaks in the gas chromatogram of the residual gases from the test samples were compared to those for ambient air. The calculations are as follows:

$$\% \text{ } O_2 \text{ in Residual Gas} = \frac{\dfrac{O_2 \text{ peak height}}{N_2 \text{ peak height}}}{\left(\dfrac{O_2 \text{ peak height}}{N_2 \text{ peak height}}\right)_{air}} \times 21.0\% \text{ } (O_2 \text{ in air})$$

$$\% \text{ } O_2 \text{ consumed} = 21.0\% - \% \text{ } O_2 \text{ in residual gas}$$

$$\text{Fraction of } O_2 \text{ consumed} = \frac{\% \text{ } O_2 \text{ consumed}}{21.0\%}$$

6.11.3.2 Oxygen Consumption Measurements - Results - Data for the fraction of oxygen consumed as a function of time at 178°C (352°F) are reported in Table 71 and Figure 36 for the three carboranes and benzene. All analyses were done in duplicate.

As judged by the consumption of available oxygen, the oxidative stability in air at 178°C (352°F) is progressively poorer in the sequence

$$(CH_3)_2B_7C_2H_7 > (CH_3)_2B_6C_2H_6 > (CH_3)_2B_5C_2H_5$$

All three of the carboranes are, however, far less resistant to oxidation than is benzene, which consumed no oxygen.

6.11.3.3 Ignition Delay Time - Method - The shock tube used to measure ignition delay (or induction) times is 3.9 cm in diameter and 3.6 meters long, equally divided lengthwise into reaction and driver sections. Incident shock speeds are measured by timing the passage of the initial shock wave between a pair of SLM model 603 pressure transducers mounted 37.5 cm apart near the downstream end of the reaction section. Gas temperatures and flow velocities are calculated from incident shock speeds.

Pressure is detected and recorded using a third SLM transducer 5 cm from the downstream end of the reaction section. Light emitted upon ignition is detected by a photomultiplier tube "looking" laterally into the shock tube through a slitted quartz window at the same axial position. Ignition delay time is taken as the interval between the detection of the pressure rise due to the reflected shock wave and the first appearance (10% of peak) of emitted light of combustion.

Table 71. COMPARISON OF FRACTION OF OXYGEN CONSUMED BY THREE CARBORANES AND BENZENE HELD AT 178°C (352°F) IN AIR FOR VARIOUS TIMES

Sample	Time (min.)	Fraction of Oxygen Consumed
Room air	0	0
	10	0
	30	0
	60	0
$(CH_3)_2B_5C_2H_5$	0	0
	10	0.28
	30	0.49
	70	0.59
	111	0.62
$(CH_3)_2B_6C_2H_6$	0	0
	10	0.20
	30	0.44
	60	0.55
$(CH_3)_2B_7C_2H_7$	0	0
	10	0.17
	30	0.28
	60	0.41
Benzene	0	0
	10	0
	30	0
	60	0

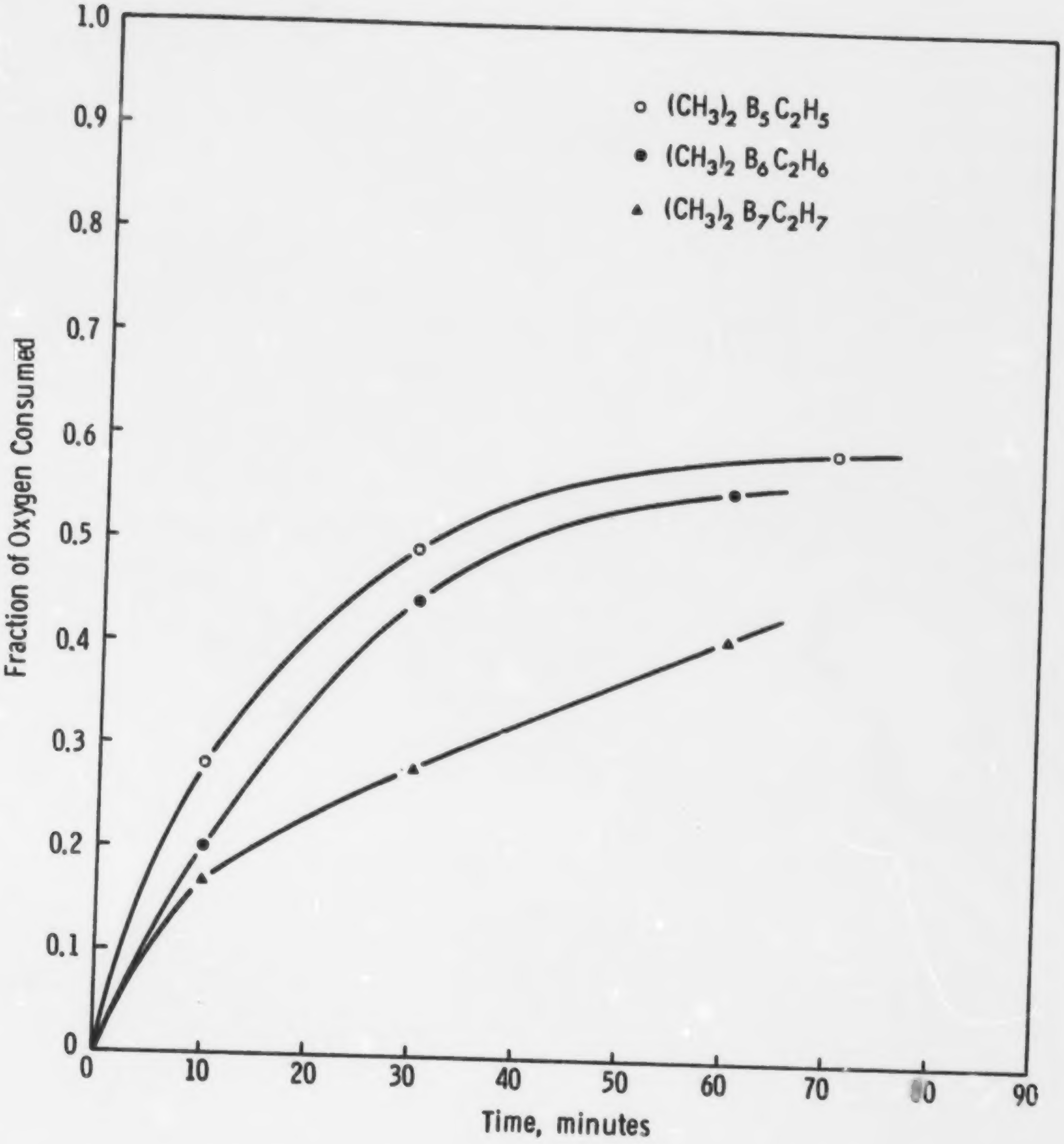

Figure 36. Comparison of Fraction of Oxygen Consumed for Carboranes Stored in Air at 178°C versus Storage Time

The "air" originally confined in the reaction section was actually a mixture of 21% oxygen and 79% argon. Into this mixture was introduced 10 microliters of the test fluid, which was then allowed to evaporate and diffuse through the mixture. The driver gas was a mixture containing 90% helium and 10% argon. By varying the initial pressures in the two halves of the shock tube, the temperature of the highly compressed "air" after shock reflection is controlled. The shock compression lasted about 5 milliseconds at a pressure near 60 psia under the conditions of the tests.

Skinner and Ruehrwein (ref. 61) give the general techniques in greater detail.

6.11.3.4 Ignition Delay Time - Results - One carborane, $(CH_3)_2B_7C_2H_7$ (the one found most resistant to oxidation in section 6.11.3.2), was chosen for comparison against two reference fluids; benzene and 1,3,5-trifluorobenzene. These were selected as representing materials "too flammable" and "marginally flammable" for the application.

Using the methods of the previous section, the results of Table 72 were obtained.

Table 72. IGNITION DELAY DATA

Sample	Shock Temp. (°K)	Ignition Delay Time (msec)	
$(CH_3)_2B_7C_2H_7$	830	0.90	
	848	1.78	
	890	0.60	
	898	0.22	
Benzene, C_6H_6	1165	1.7	
	1165	1.6	
	1288	0.4	
	1367	0.1	
	1392	0.1	
1,3,5-Trifluorobenzene, $C_6H_3F_3$	1367	>5	No ignition
	1397	>5	
	1402	>5	
	1559	>5	

The data of this table are plotted in traditional Arrhenius form in Figure 37 where the least-mean-square fitted curves correspond to the relation

$$\tau = A \exp(B/T). \qquad (22)$$

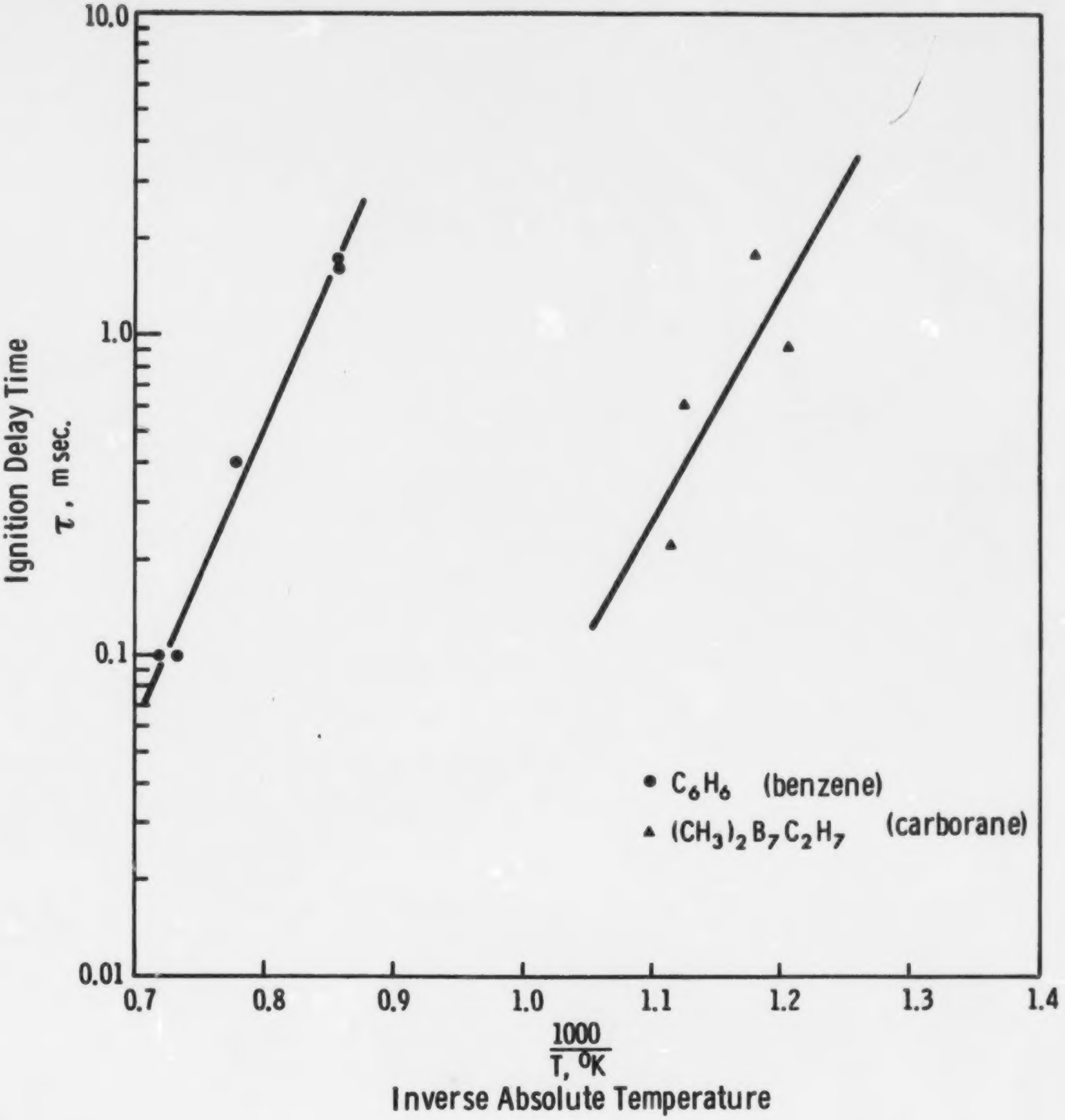

Figure 37. Ignition Delay Times - Carborane and Reference Fluid

This figure clearly shows that the ignition delay time of the carborane is about 1/300 the delay time of benzene at any particular temperature. At a particular delay time, the corresponding ignition temperature of the carborane is about 350°K lower than benzene. Either way, it is clear that the carborane is much more readily ignited in "air" than is benzene. Benzene in turn is much more readily ignited than trifluorobenzene. Under the test conditions, the trifluorobenzene never did ignite within the 5 millisecond span of the compression.

6.11.4 Inorganic Fluids

Many covalent inorganic fluids exist which have boiling points in the range desired for the present application. Examples of these are listed in Table 73. It is tempting to seek useful fluids within this class of materials. Closer investigation, however, reveals that without exception fluids of the types shown are so extremely reactive (corrosive) and/or noxious that they cannot be considered in any application involving contact(s) with materials ordinarily used in automotive construction. To prove this point, 24-hour ampoule tests (at 720°F) were run on phosphorus oxychloride ($POCl_3$) and germanium tetrachloride ($GeCl_4$). As expected, the fluids survived the thermal stress easily but the SAE 1008 steel ampoules were very extensively corroded inside. Despite extensive literature search and consultation with outside authorities, no inorganic fluids of any promise could be identified.

Table 73. SOME UNCONVENTIONAL INORGANIC FLUIDS

Material	Melting Point (°C)	Boiling Point (°C)
$AsCl_3$	- 8.5	63
CSe_2	-45.5	126
$CSSe$	-85	84
CrO_2Cl_2	-96.5	117
$O{=}P(OH)F_2$	-75	116
GeH_2Br_2	-15	89
GeH_2Cl_2	-68	69.5
$GeCl_4$	-49	84
$Fe(CO)_5$	21	103
PCl_3	-112	76
$POBrCl_2$	13	138
$POCl_3$	2	105
$PSCl_3$	-35	125
ReO_3Cl	4.5	131
$SeOF_2$	4.6	124
SiH_2Br_2	-70.1	66
$SiHBr_3$	-73	109
$SiBr_2Cl_2$	-45	104
$SiBr_3Cl$	-28	128
$SiCl_3F$	-60	113
$SiBr_4$	5.4	154
$SiCl_4$	-70	56
Si_2Cl_6	- 1	145
Si_4H_{10}	-108	84
$Cl_3SiOSiCl_3$	28	137
S_2Cl_2	-80	136
SO_2Cl_2	-54	69
$SOCl_2$	-105	79
$SnCl_4$	-33	114
$TiCl_4$	-25	136
UF_5	--	111
$VOCl_3$	-77	127

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